

I. INTRODUCTION TO THE SECTOR NOTEBOOK PROJECT

I.A. Summary of the Sector Notebook Project

Integrated environmental policies based upon comprehensive analysis of air, water and land pollution are a logical supplement to traditional single-media approaches to environmental protection. Environmental regulatory agencies are beginning to embrace comprehensive, multi-statute solutions to facility permitting, enforcement and compliance assurance, education/outreach, research, and regulatory development issues. The central concepts driving the new policy direction are that pollutant releases to each environmental medium (air, water and land) affect each other, and that environmental strategies must actively identify and address these inter-relationships by designing policies for the “whole” facility. One way to achieve a whole facility focus is to design environmental policies for similar industrial facilities. By doing so, environmental concerns that are common to the manufacturing of similar products can be addressed in a comprehensive manner. Recognition of the need to develop the industrial “sector-based” approach within the EPA Office of Compliance led to the creation of this document.

The Sector Notebook Project was originally initiated by the Office of Compliance within the Office of Enforcement and Compliance Assurance (OECA) to provide its staff and managers with summary information for eighteen specific industrial sectors. As other EPA offices, states, the regulated community, environmental groups, and the public became interested in this project, the scope of the original project was expanded to its current form. The ability to design comprehensive, common sense environmental protection measures for specific industries is dependent on knowledge of several inter-related topics. For the purposes of this project, the key elements chosen for inclusion are: general industry information (economic and geographic); a description of industrial processes; pollution outputs; pollution prevention opportunities; federal statutory and regulatory framework; compliance history; and a description of partnerships that have been formed between regulatory agencies, the regulated community and the public.

For any given industry, each topic listed above could alone be the subject of a lengthy volume. However, in order to produce a manageable document, this project focuses on providing summary information for each topic. This format provides the reader with a synopsis of each issue, and references where more in-depth information is available. Text within each profile was researched from a variety of sources, and was usually condensed from more detailed sources pertaining to specific topics. This approach allows for a wide coverage of activities that can be further explored based upon the citations and references listed at the end of this profile. As a check on the information included, each notebook went through an external review process. The Office of Compliance appreciates the efforts of all those that participated

in this process who enabled us to develop more complete, accurate and up-to-date summaries. Many of those who reviewed this notebook are listed as contacts in Section IX and may be sources of additional information. The individuals and groups on this list do not necessarily concur with all statements within this notebook.

I.B. Additional Information

Providing Comments

OECA's Office of Compliance plans to periodically review and update the notebooks and will make these updates available both in hard copy and electronically. If you have any comments on the existing notebook, or if you would like to provide additional information, please send a hard copy and computer disk to the EPA Office of Compliance, Sector Notebook Project (2223-A), 1200 Pennsylvania Avenue, NW, Washington, DC 20460. Comments can also be uploaded to the Enviro\$en\$e World Wide Web for general access to all users of the system. Follow instructions in Appendix A for accessing this system. Once you have logged in, procedures for uploading text are available from the on-line Enviro\$en\$e Help System.

Adapting Notebooks to Particular Needs

The scope of the industry sector described in this notebook approximates the national occurrence of facility types within the sector. In many instances, industries within specific geographic regions or states may have unique characteristics that are not fully captured in these profiles. The Office of Compliance encourages state and local environmental agencies and other groups to supplement or repackage the information included in this notebook to include more specific industrial and regulatory information that may be available. Additionally, interested states may want to supplement the "Summary of Applicable Federal Statutes and Regulations" section with state and local requirements. Compliance or technical assistance providers may also want to develop the "Pollution Prevention" section in more detail. Please contact the appropriate specialist listed on the opening page of this notebook if your office is interested in assisting us in the further development of the information or policies addressed within this volume. If you are interested in assisting in the development of new notebooks for sectors not covered in the original eighteen, please contact the Office of Compliance at 202-564-2310.

II. INTRODUCTION TO THE AGRICULTURAL CHEMICAL INDUSTRY

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the fertilizer, pesticide, and agricultural chemical industry. Facilities described within this document are described in terms of their Standard Industrial Classification (SIC) codes whenever possible.

II.A. Introduction, Background, and Scope of the Notebook

The scope of this Sector Notebook covers the manufacturing and production of fertilizers, the formulation of pesticide chemicals (both agricultural and non-agricultural) manufactured at separate facilities, and the production of other miscellaneous agricultural chemicals. It does not include the use, sale, distribution, or storage of such chemicals.

The Fertilizer, Pesticide, and Agricultural Chemical Industry is classified by the Office of Management and Budget (OMB) under Standard Industrial Classification (SIC) Industry Group Number 287. This classification corresponds to SIC codes which were established by the OMB to track the flow of goods and services within the economy. Industry Group Number 287 includes SIC codes:

- 2873-- Nitrogenous Fertilizers
- 2874-- Phosphatic Fertilizers
- 2875-- Fertilizers, Mixing Only
- 2879-- Pesticides and Agricultural Chemicals, Not Elsewhere Classified (n.e.c)

This notebook covers both fertilizer manufacturing and formulating operations including ammonia synthesis, nitric and phosphoric acid production, and the mixing, preparing, and packaging of nitrogenous and phosphatic fertilizers. Establishments engaged in manufacturing fertilizer materials or mixing fertilizers produced at the same establishment are classified under SIC codes 2873 and 2874. Mixing of fertilizer materials, such as compost, potting soil, and fertilizers made in plants not manufacturing fertilizer materials, is classified under SIC code 2875. This notebook does not include the mining or grinding of phosphate rock, which is classified under SIC code 1475, and it also does not include the use or application of fertilizers.

SIC code 2879, pesticides and agricultural chemicals not elsewhere classified (n.e.c.), hereafter referred to as pesticides and miscellaneous agricultural chemicals, covers only the formulating, preparing, and packaging of ready-to-use agricultural and household pest control chemicals. This industry code also includes establishments primarily engaged in the manufacturing or formulating of agricultural chemicals, not elsewhere classified, such as minor or trace elements and soil conditioners. This notebook does not discuss the use or

application of pesticide products. Establishments primarily engaged in the manufacturing of basic or technical agricultural pesticides are classified in Industry Group 281 if the chemicals produced are inorganic or Industry Group 286 if the chemicals produced are organic. This notebook also does not cover the agricultural supply sector, SIC 5191, which is engaged in the wholesale and distribution of various agricultural supplies including fertilizers and pesticides. Also, there is little discussion of the potassium fertilizer industry as potash is classified under SIC 2819, Inorganic Chemicals n.e.c.

Federal government agencies, including United States EPA, are beginning to implement an industrial classification system developed by OMB to replace the SIC code system. The new system, which is based on similar production processes, is called the North American Industrial Classification System (NAICS). In the NAIC system, the manufacturing of nitrogenous fertilizers (SIC 2873) is classified as NAIC 325311, phosphatic fertilizers (SIC 2874) as NAIC 325312, and fertilizer mixing only (SIC 2875) as NAIC 325314. Pesticide formulating and agricultural chemicals n.e.c. (SIC 2879) is classified under NAIC 32532. Because EPA databases, and other databases used in this document, are still using the SIC system, the industry sectors described in this Sector Notebook are described in terms of their SIC codes.

II.B. Characterization of the Fertilizer, Pesticide, and Agricultural Chemical Industry

As the world population increases, crop lands are unable to meet the growing demand for food without employing some method of crop enhancement. There are five common practices used to meet the growing demand:

- C increasing tilled acreage
- C improving plant strains
- C introducing or expanding irrigation
- C controlling pest by chemical or biological methods
- C initiating or increasing fertilizer usage

Increased utilization of the last two methods has created a large agrichemical industry which produces a wide variety of products designed to increase crop production and protect crops from disease and pests (Kent, 1992). Together, the production of fertilizers and the formulation of pesticides was a \$18.8 billion industry in 1992, employing over 40,000 people (USDOD, 1995).

Plants require 18 elements to grow, the most important being oxygen, carbon, hydrogen, nitrogen, phosphorous, and potassium. Oxygen, carbon, and hydrogen are obtained from the atmosphere and water, while nitrogen, phosphorous, and potassium are naturally obtained from soil. However, under current high yield production methods, soils are stripped of the essential nutrients, requiring the addition of fertilizers (primarily consisting of nitrogen, phosphorous, and potassium) to resupply the land. The additional 12 essential nutrients are generally maintained in soil at sufficient levels for plant growth,

but they may be added to some fertilizers (Kent, 1992).

Even before the addition of nutrients to farm lands, farmers were forced to protect their crops against pests with chemicals. References to pesticide usage date back to 1000 B.C. Pests are continuously adapting to pesticide chemicals requiring new pesticides and the usage of multiple chemical agents. The industry is rapidly changing due to biological adaptation of pests, laboratory discoveries, and government regulation (Kent, 1992). The pesticide industry is faced with the need for new formulations and the abundance of possible combinations, but restricted by cost factors and a sometimes lengthy registration process.

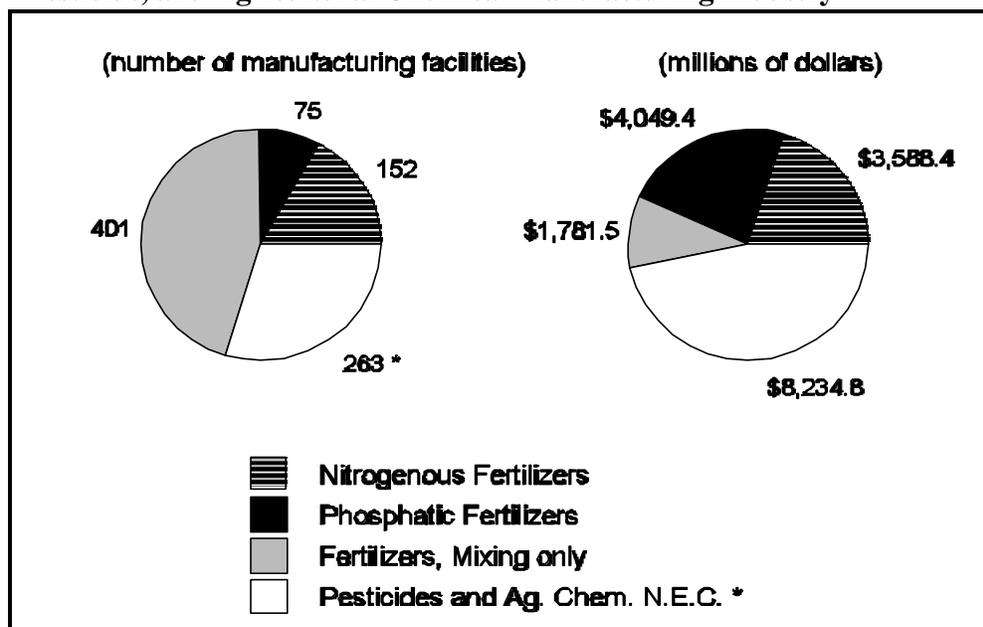
Pesticides are applied on about three-quarters of United States farms and households. Farmers' expenditures on pesticides were equal to 4.6 percent of total farm production expenditures in 1995, up from 3.9 percent in 1993. About one billion pounds of active ingredient of conventional pesticides are used annually in the United States; this usage involves about 21,000 pesticide products (including non-agricultural products) and 875 active ingredients registered under the Federal Pesticide Law, according to the *1994 and 1995 Market Estimates for Pesticides Industry Sales and Usage* (Aspelin, 1997).

II.B.1. Product Characterization

This notebook covers all aspects of fertilizer production and pesticide formulating and packaging. However, because the industrial processes, pollutant outputs, economics, size, and geographic distribution of the two industries are different, they are dealt with separately throughout the notebook.

Figure 1 compares the number of manufacturing facilities and value of shipments for each of the major sectors within the Fertilizer, Pesticide, and Agricultural Chemical Industry, as reported by the United States Bureau of Census. The figure shows that the fertilizer mixing industry has the largest number of facilities but the smallest value of shipments. This reflects that, compared to other sub-sectors within the Fertilizer, Pesticide and Agricultural Chemical Industry, these facilities produce a relatively small volume of product and sell a relatively low value product. Phosphatic fertilizer producers, on the other hand, comprise the smallest number of facilities but have a relatively large share of the industry's value of shipments, reflecting that individual facilities produce a relatively large volume of product.

Figure 1: Number of Facilities and Value of Shipments of the Fertilizer, Pesticide, and Agricultural Chemical Manufacturing Industry



Source: 1992 Census of Manufacturers, Industry Series: Agricultural Chemicals, United States Department of Commerce, Bureau of the Census, May 1995.

* United States EPA has identified over 8,000 establishments that could fall within this SIC code as it is defined by the OMB. See discussion in text below.

The Census of Manufacturers reports 263 establishments that can be defined as producing pesticides and miscellaneous agricultural chemicals. These establishments reportedly account for almost half of the value of shipments for the sector. There are over 8,000 establishments identified by the United States EPA that manufacture, formulate and package pesticides and other agricultural chemicals and that could fall within OMB's SIC code definition for this sector. Many of these are small establishments and establishments that have a primary line of business other than producing pesticides and other miscellaneous agricultural chemicals. The Census only counts those facilities which report an SIC code as their primary line of business, thus the number of facilities shown above is not inclusive of all facilities involved in agricultural chemical production. Under the "Pesticides and Miscellaneous Agricultural Chemicals" heading later in this section, other pesticide producing establishment counts are presented based on EPA estimates and reporting under section 7 of the Federal Insecticide, Fungicide, and Rodenticide Act.

Nitrogenous Fertilizers

The nitrogenous fertilizer industry includes the production of synthetic ammonia, nitric acid, ammonium nitrate, and urea. Synthetic ammonia and nitric acid, however, are used primarily as intermediates in the production of ammonium nitrate and urea fertilizers. Table 1 lists specific products classified as nitrogenous fertilizers by OMB.

**Table 1: Nitrogenous Fertilizer Products
(SIC 2873)**

Ammonia liquor Ammonium nitrate Ammonium sulfate Anhydrous ammonia Aqua ammonia Fertilizers, mixed, produced in nitrogenous fertilizer plants Fertilizers, natural Nitric acid Nitrogen fertilizer solutions Plant foods, mixed in nitrogenous fertilizer plants Urea

Source: Standard Industrial Classification Manual, Office of Management and Budget, 1987.

Synthetic Ammonia

Synthetic ammonia refers to ammonia that has been synthesized from natural gas. In this process, natural gas molecules are reduced to carbon and hydrogen. The hydrogen is then purified and reacted with nitrogen to produce ammonia. Approximately 75 percent of the synthetic ammonia produced in the United States is used as fertilizer, either directly as ammonia or indirectly after fertilizer synthesis into urea, ammonium nitrate, and monoammonium or diammonium phosphates. One-third of the fertilizer nitrogen is applied directly to the land as anhydrous ammonia. The remaining 25 percent of ammonia produced in the United States is used as raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products (USEPA, 1993a).

Nitric Acid

Nitric acid is formed by concentration, absorption, and oxidation of anhydrous ammonia. About 70 percent of the nitric acid produced is consumed as an intermediate in the manufacture of ammonium nitrate (NH_4NO_3), which is primarily used in fertilizers. Another 5 to 10 percent of the nitric acid produced is used in adipic acid manufacturing, an intermediate in nylon production. Explosive manufacturing utilizes nitric acid for organic nitrations to produce nitrobenzene, dinitrotoluenes, and other chemical intermediates. Other end uses of nitric acid are gold and silver separation, military munitions,

steel and brass pickling, photoengraving, and acidulation of phosphate rock (USEPA, 1993a).

Ammonium Nitrate

Ammonium nitrate is produced by neutralizing nitric acid with ammonia. Approximately 15 to 20 percent of ammonium nitrate is used for explosives and the balance for fertilizer. Ammonium nitrate is marketed in several forms, depending upon its use. Liquid ammonium nitrate may be sold as a fertilizer, generally in combination with urea. Liquid ammonium nitrate may also be concentrated to form an ammonium nitrate "melt" for use in solids formation processes. Solid ammonium nitrate may be produced in the form of prills, grains, granules or crystals. Prills, round or needle-shaped aggregates, can be produced in either high or low density form, depending on the concentration of the melt. High density prills, granules and crystals are used as fertilizer, grains are used solely in explosives, and low density prills can be used as either fertilizer or explosives (USEPA, 1993a).

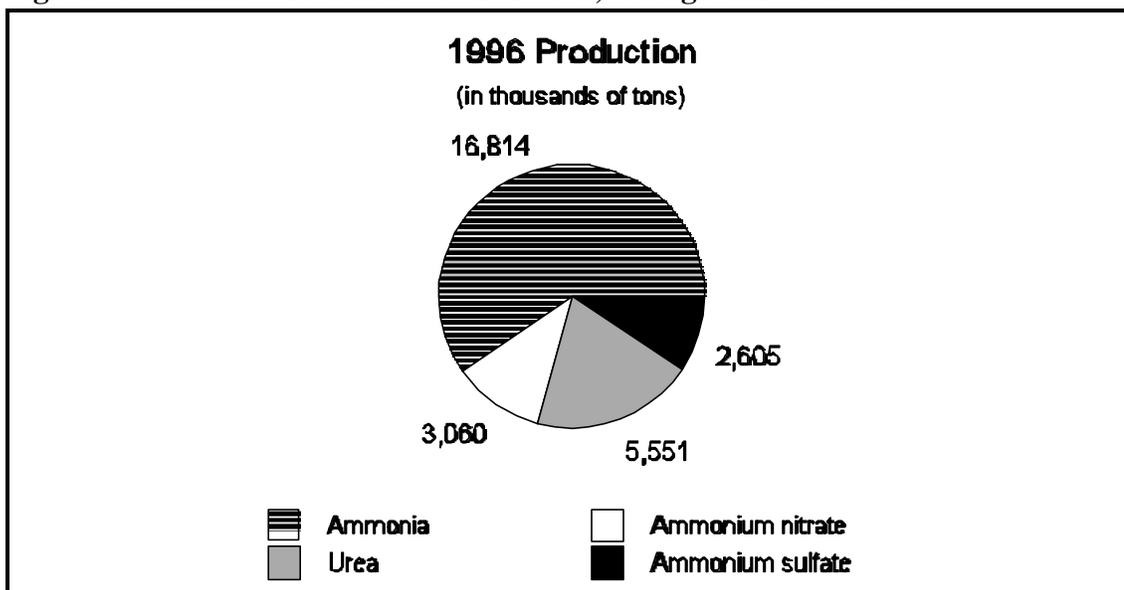
Urea

Urea, also known as carbamide or carbonyl diamide, is produced by reacting ammonia with carbon dioxide. Eighty-five percent of urea solution produced is used in fertilizer mixtures, with three percent going to animal feed supplements and 12 percent is used for plastics and other uses. Urea is marketed as a solution or in solid form. Most solids are produced as prills or granules for use as fertilizer or protein supplement in animal feed, and in plastics manufacturing (USEPA, 1993a).

Ammonium sulfate

It is not economically feasible to produce ammonium sulfate for use as a fertilizer. However, ammonium sulfate is formed as a by-product of other process such as acid scrubbing of coke oven gas, synthetic fiber production, and the ammoniation of process sulfuric acid (Hoffmeister, 1993). Therefore, the production of ammonium sulfate is not described in this notebook.

Figure 2: Product Distribution for SIC 2873, Nitrogenous Fertilizers



Source: Fertilizer Institute data as reported in *Chemical and Engineering News*, June 23, 1998. Figures are based on Fertilizer Institute surveys and may not represent the entire industry.

Phosphatic Fertilizers

The phosphatic fertilizer industry can be divided into three major segments: phosphoric acid, granular ammonium phosphate, and normal and triple superphosphate. Table 2 lists these, and a few additional, less common products classified as phosphatic fertilizers by OMB.

Table 2: Phosphatic Fertilizer Products (SIC 2874)
Ammonium phosphates
Calcium meta-phosphates
Defluorinated phosphates
Diammonium phosphates
Fertilizers, mixed, produced in phosphatic fertilizer plants
Phosphoric acid
Plant foods, mixed in phosphatic fertilizer plants
Superphosphates, ammoniated and not ammoniated
<i>Source: Standard Industrial Classification Manual, Office of Management and Budget, 1987.</i>

Phosphoric Acid

Phosphoric acid (H_3PO_4) can be manufactured using either a wet or a thermal process to react phosphate rock with sulfuric acid. Approximately 96 percent of the phosphoric acid produced in the United States is produced using the wet process. Wet process phosphoric acid has a phosphorous concentration typically ranging from 26-30% as phosphorous pentoxide (P_2O_5) and is used in the production of ammonium phosphates and triple superphosphates. Thermal process phosphoric acid is commonly used in the manufacture of high grade chemicals requiring a much higher purity.

Ammonium Phosphates

Ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphatic fertilizers are produced in the United States. The most common ammonium phosphatic fertilizer grades are monoammonium phosphate (MAP) and diammonium phosphate (DAP). DAP has become one of the most commonly used fertilizers because it provides a large quantity of plant food, is compatible with most mix fertilizer ingredients, and is nonexplosive. It may be directly applied or used in irrigation systems as it is completely soluble in water. DAP is also preferred over MAP because it is capable of fixing twice as much ammonia per phosphorous pentoxide in solid form (Nielson, 1987.) MAP contains a higher concentration of phosphorous pentoxide than DAP. It is favored for use with alkaline soils and may be applied either directly or in a dry blend.

Normal Superphosphates

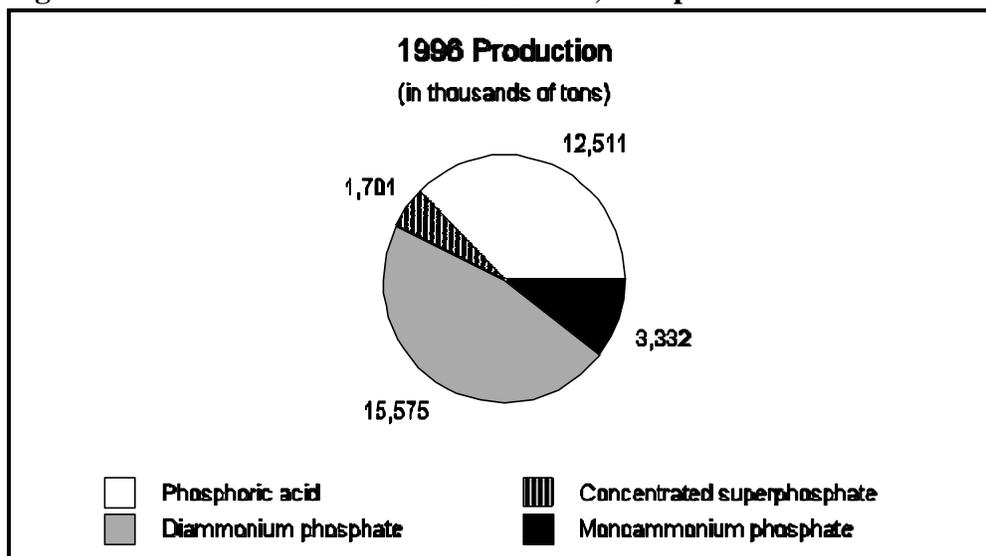
Like phosphoric acid, normal, or "ordinary," superphosphate fertilizers are produced by reacting phosphate rock with sulfuric acid. However, normal superphosphate (NSP) retains calcium sulfate which forms by the reaction between phosphate rock and sulfuric acid. For this reason NSP retains its importance wherever sulphur deficiency limits crop yields (UNEP, 1996). NSP refers to fertilizer material containing 15 to 21 percent phosphorous as phosphorous pentoxide (P_2O_5). As defined by the Census Bureau, NSP contains not more than 22 percent of available P_2O_5 (USEPA, 1993a). Production of NSP has given way to the higher-yielding triple superphosphates and ammonium phosphates. In 1990, production of NSP accounted for only one percent by weight of the phosphorous fertilizer industry. Because of its low P_2O_5 concentration, shipping can be prohibitively expensive due to the large volumes required. NSP is favored in low cost Nitrogen-Phosphorous-Potassium (NPK) mixes because it is a less expensive form of phosphorous, however, it is unacceptable for higher-grade mixes (Kent, 1992).

Triple Superphosphates

Triple superphosphates (TSP) are produced by reacting ground phosphate rock with phosphoric acid. Triple superphosphate is also known as double, treble, or concentrated superphosphate. The phosphorus content of triple superphosphates is over 40 percent, measured as phosphorus pentoxide (P_2O_5),

which is its main advantage over other phosphatic fertilizers (USEPA, 1993a). TSP began to be produced in large quantities when wet process phosphoric acid production became available commercially. It is commonly produced along with phosphoric acid near phosphate rock supplies. TSP may be applied directly or as a bulk blend (Kent, 1992).

Figure 3: Product Distribution for SIC 2874, Phosphorous Fertilizers



Source: Chemical and Engineering News, June 23, 1998. Figures are based on Fertilizer Institute surveys and may not represent the entire industry.

Fertilizers, Mixing Only

A significant part of the fertilizer industry only purchases fertilizer materials in bulk from fertilizer manufacturing facilities and mixes them to sell as a fertilizer formulation.

Phosphorous is the single nutrient most likely to be applied in a fertilizer mixture, as seen in Table 3.

Table 3: 1990 Direct vs Mixed Application of Primary Fertilizer Nutrients

Nutrient	Method, % applied	
	Direct	Mixtures
Nitrogen	80	20
Phosphorous	8	92
Potassium	65	35
TOTAL	61	39

Source: Hoffmeister, G., "Fertilizers," Kirk-Othmer Encyclopedia of Chemical Technology, V. 10, 1993.

Although the Bureau of the Census only counts 401 facilities reporting the SIC code for fertilizer mixing (2875) in 1992, other sources estimated the true number of fertilizer mixing facilities to be closer to five or six thousand in 1984 (Adrienas and Vroomen, 1990). About half of applied fertilizers are bulk blends. Fertilizer mixing facilities generally serve a small area such as farms within a ten to fifty mile radius. The processes involved are simple and relatively little value is added to the raw materials purchased by mixing facilities. Nevertheless, there are many of these facilities and volume of production results in a \$1.8 billion industry (value of annual shipments). The industrial process is simple and resembles that of the pesticide formulating sector. A brief discussion of fertilizer mixing processes is included in this notebook.

Pesticides and Miscellaneous Agricultural Chemicals

The pesticides and agricultural chemicals n.e.c. (referred to here as pesticides and miscellaneous agricultural chemicals) industry group (SIC 2879) formulates and prepares ready to use agricultural and household pesticides and other agricultural chemicals. The manufacture of pesticide active ingredients is classified under either Industry Group 281 for inorganic chemicals or 286 for organics which are not covered by this notebook. (*See Profile of the Inorganic Chemicals Industry and Profile of the Organic Chemicals Industry Sector Notebooks.*) In the United States, over 850 different pesticide formulations and preparations are produced. In 1995, 31 new active ingredients were registered in the United States (Aspelin, 1997). Most of these pesticides can be classified as either insecticides, herbicides, or fungicides, although many other minor classifications exist. Also included in this category are blends of fertilizers and pesticides produced at pesticide formulating and

mixing facilities. Table 4 lists the pesticides and other products included in SIC 2879.

Table 4: SIC 2879 Pesticides and Miscellaneous Agricultural Chemicals, List of Products

Agricultural disinfectants	Insecticides, agricultural and household	Poison, household
Agricultural pesticides	Lime-sulfur, dry and solution	Pyrethrin
Arsenates and arsenites	Lindane, formulated	Rodenticides
Bordeaux mixture	Moth repellants	Rotenone
Cattle dips and sheep dips	Nicotine and salts	Soil conditioners
DDT	Paris green	Sulfur dust
Defoliants	Pesticides, household	Thiocyanates
Fly sprays	Phytoactin	Trace elements (agricultural)
Fungicides	Plant hormones	Xanthone
Growth regulators		
Herbicides		

Source: Standard Industrial Classification Manual, Office of Management and Budget, 1987.

In 1995, 77 percent (by volume) of all pesticides were used for agriculture, 12 percent for industrial, commercial, or governmental lands or facilities, and 11 percent for homes and gardens (Aspelin, 1997). Non-agricultural pesticides and miscellaneous agricultural chemicals are included in the data presented for sales, production, waste management, and enforcement and compliance. However, since they represent a relatively small part of the industry and cover a wide range of chemicals and production processes, these products are not covered in the Industrial Processes and Pollutant Outputs sections of this document.

Herbicides

Herbicides (in both value and quantity) are the largest class of pesticides used in the United States, as well as in the world. This class of pesticides, which accounts for approximately fifty percent of the value of aggregate world pesticide usage, is used to destroy or control a wide variety of weeds and other unwanted plants. Because of its demonstrated farm labor savings, nearly all the agricultural land in the United States is currently being treated with some type of herbicide. In recent years, approximately fifty percent of total United States pesticide consumption (by value) was herbicides (USITC, 1994).

Insecticides

Insecticides are the second largest pesticide category (by value) used in the United States and in the world. In the early 1990s, insecticides accounted for approximately twenty-nine percent of the total value of United States pesticide consumption. Historically, the category of synthetic organic insecticides has been divided into one of four major chemical groups:

- C organochlorines (e.g., DDT and chlordane)

- C organophosphates (e.g., parathion and diazinon)
- C carbamates (e.g., carbaryl)
- C pyrethroids (e.g., natural and synthetic)

Several compounds, discovered during the 1950s, found widespread use in agriculture because of their high toxicity to a variety of insects. However, the qualities that made these chemicals so desirable also led to their eventual removal from the market, as these products also proved harmful to humans and to the environment. Spurred in part by increased environmental concern, researchers developed a new series of less toxic synthetic compounds called pyrethroids. These compounds are based on the natural pyrethroids, which are found in such plants as the chrysanthemum (USITC, 1994).

Fungicides

In recent years, fungicides accounted for approximately ten percent of the value of total United States pesticide consumption. Fungicides are used today primarily to protect agricultural crops and seeds from various fungi; farmers previously used inorganic products, such as elemental sulfur and copper sulfate. Initially, synthetic products were commercially unsuccessful, because of their high manufacturing costs. By the 1940s, however, newer, less expensive products became commercially successful. Today, fungicides are manufactured from a variety of chemical classes. Commercially, the most important fungicides are halogenated compounds, the carbamates and dithiocarbamates, and organophosphates (USITC, 1994).

Other Pesticides

Although small in total quantity consumed, a number of other classes of pesticide products are on the market. Some of these pesticides are not covered by this Notebook.

- C **Biological pesticides**, also known as biopesticides, include true biological agents, living or reproduced biological entities such as viruses or bacteria, and naturally occurring biochemicals such as plant growth regulators, hormones, and insect sexual attractants (pheromones) that function by modes of action other than innate toxicity. At the end of 1998, there were approximately 175 registered biopesticide active ingredients and 700 products. Generally, biological pesticides pose little or no risk to human health or the environment. Accordingly EPA generally requires much less data to register a biopesticide than to register a conventional pesticide (USEPA, 1999). To further facilitate the registration of biopesticides, in 1994, EPA established the Biopesticides and Pollution Prevention Division in the Office of Pesticide Programs.
- C **Plant growth regulators** have been developed by many companies to improve crop production. Plant growth regulators are produced for a variety of purposes, including loosening ripened fruits for faster harvest; controlling the size and firmness of fruits; and regulating the size of a plant

to increase branching. These products account for a small portion of world and United States usage. Future development will probably be directed toward selected crops for which the application of these specialty products is found to be the most cost effective (USITC, 1994).

- C **Sex attractants** may be used to attract insects to traps or to confuse specific male insects, making it difficult to locate females for mating. Commercially available sexual attractants are synthetically produced compounds. Insect growth regulators, such as juvenile growth hormones, are synthetic compounds similar to the natural chemicals that regulate insect growth.
- C **Genetically modified plants** are plants developed through the use of biotechnology. There are three types of plants that are relevant to pest control: herbicide-tolerant plants (which can tolerate certain types of herbicides), insect-resistant plants (which can withstand attacks by certain insects), and virus- and other pest-resistant plants (which are immune to some types of plant viruses and other plant pests). As of September 1994, several genetically modified plants had been commercialized and had elicited optimism that genetically modified plants would become an important new approach to controlling pests (USDA, 1995).

The environmental benefits of reduced use of chemical pesticides are also significant. Environmental side effects of traditional pesticides include the cost of providing alternative sources of drinking water, increased treatment costs for public and private water systems, lost boating and swimming opportunities, worker safety concerns, exposure to nearby residents, increased exposures for farm children, possible loss of biodiversity, pressure on threatened and endangered species, and damage to recreational and fishery resources (USDA, 1995).

Pesticide Formulations

Pesticide formulations may exist in any of the three following physical states: liquid, dry, and pressurized gas. The liquid formulation may be applied directly in liquid form or propelled as an aerosol. Some common dry-based formulations are dusts, wettable powders, granules, treated seed, bait pellets, encapsulated, and cubes. Pressurized gas formulations are used primarily for soil fumigation (USEPA, 1996). Gaseous pesticides can be subjected to high pressures which often convert the formulation to a liquid which can be stored, transported and applied from gas cylinders.

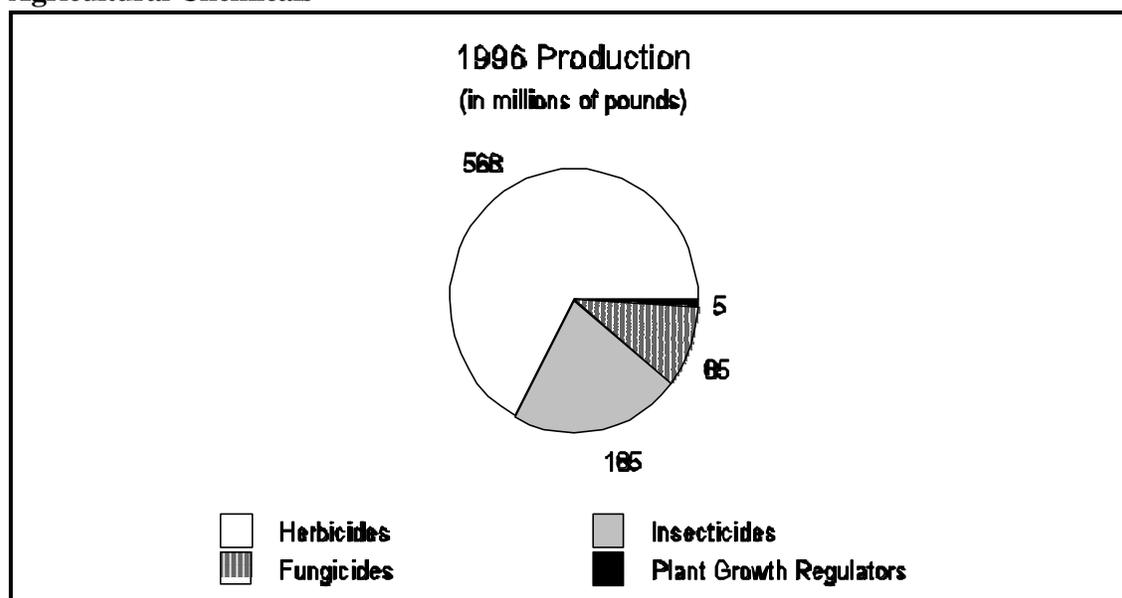
Repackaging of pesticide formulations is common when materials are to be transferred from bulk storage to a smaller scale of packaging for use by a consumer. Products are typically repackaged in smaller containers and consumer-specific labeling is added (USEPA, 1996).

In 1995, roughly 79 percent of all pesticides were used on agricultural

cropland. The remainder were used in private homes and gardens and on commercial and industrial property (Aspelin, 1997). Therefore, although non-agricultural pesticides are included in SIC code 2879 and thus the notebook, the specific packaging or formulating requirements of those products are not included. However, the sales, production, pollutant releases, and enforcement and compliance data reflect non-agricultural pesticides as well as agricultural pesticides.

The majority of pesticides were used on only a few major crops: cotton, corn, soybeans, and apples. The major pesticide chemicals used in United States agricultural crop production are atrazine, metolachlor, metamsodium, methyl bromide¹, and dichloropropene (Aspelin, 1997).

Figure 4: Product Distribution for SIC 2879, Pesticides and Miscellaneous Agricultural Chemicals



Source: American Crop Protection Association, as reported in *Chemical and Engineering News*, June 23, 1998.

Establishment Reporting Under FIFRA Section 7

Information reported under section 7 of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) is another source of facility level data for the pesticides

¹ Production and importation of methyl bromide is currently being phased out. It will be reduced from 1991 levels and will be completely phased out in 2005.

industry. All establishments that produce pesticides in the United States or that import pesticides into the United States are required to register and report their production volume to the EPA. These data differ from the Census of Manufacturers data presented above for the agricultural chemical industry as a whole. The Census of Manufacturers data only covers facilities that are manufacturing these products, while the FIFRA data system more broadly includes establishments that “produce” these products. The term, “produce” has been defined under FIFRA and 40 CFR Part 167 to mean “to manufacture, prepare, propagate, compound, or process any pesticide, including any pesticide produced pursuant to section 5 of FIFRA, any active ingredient, or device, or to package, repackage, label, relabel, or otherwise change the container of any pesticide or device.” Repackaging or otherwise changing the container of any pesticide or device in bulk amounts constitutes pesticide production. Under FIFRA section 7, products are reported under one of four product types:

- 1) Technical material or active ingredient
- 2) End-use blend, formulation, or concentrate
- 3) Repackaged or relabeled product
- 4) Device

The total number of establishments, domestic and foreign, that reported to EPA under FIFRA section 7 are presented in Table 5. Although there are approximately twelve to thirteen thousand Active Registered Pesticide-Producing Establishments, table 5 below only lists establishments that reported actual production for the calendar year 1996. The establishments that reported either zero production or who were non-reporters for calendar year 1996 are not included in the establishment number totals in the table. The significant difference between the pesticide producing establishment counts as reported under section 7 (8,612) and the pesticide and agricultural chemical manufacturers n.e.c. reported by the Census (263) can be attributed to the section 7 broad inclusion of producers vs. the relatively narrow, Census inclusion of manufacturers. In addition, the Census of Manufacturers uses SIC code definitions which lump many pesticide active ingredient manufacturers into SIC codes that represent organic or inorganic chemicals. Establishments classified under the first product type, as well as some of the second, may include facilities classified under the chemical manufacturing SIC codes 286 or 281. Also, the Census only counts a facility in an SIC code if they report a product in that SIC code as their primary line of business. Therefore, facilities producing a variety of products might not be classified under all applicable SIC codes. For example, a facility which produces many different types of fertilizers as well as some pesticides might only be counted under the fertilizer SIC codes by the Census Bureau to avoid double counting of facilities.

Type	Product	Total	Domestic	Foreign
1	Technical Material, Active Ingredient	555	410	145
2	End-Use Blend, Formulation, Concentrate	2,590	2,454	136
3	Repackaged or Relabeled Goods	5,267	5,243	24
4	Devices	200	166	34
Total		8,612	8,273	339

Source: U.S.EPA, Enforcement, Planning, Targeting & Data Division,, FIFRA, section 7 Data System, United States EPA. 1996.

II.B.2. Industry Size and Geographic Distribution

Table 6 lists the facility size distribution within the nitrogenous fertilizer, phosphatic fertilizer, fertilizer mixing, and pesticide and agricultural chemical formulating industries. For each industry code, the majority of facilities employ less than 50 people.

Table 6: Facility Size Distribution for the Fertilizer, Pesticide, and Agricultural Chemical Manufacturing Industry								
Employees per Facility	FERTILIZERS						PESTICIDES	
	Nitrogenous Fertilizers (SIC 2873)		Phosphatic Fertilizers (SIC 2874)		Fertilizers, Mixing only (SIC 2875)		Pesticides and other Agrichemicals (SIC 2879)*	
	Number of Facilities	Percentage of Facilities	Number of Facilities	Percentage of Facilities	Number of Facilities	Percentage of Facilities	Number of Facilities	Percentage of Facilities
1-9	60	39%	27	36%	205	51%	108	41%
10-49	47	31%	22	29%	166	41%	95	36%
50-249	43	28%	15	20%	30	8%	45	17%
250-499	1	1%	6	8%	0	0%	7	3%
500-2499	1	1%	5	7%	0	0%	8	3%
Total	152	100%	75	100%	401	100%	263*	100%

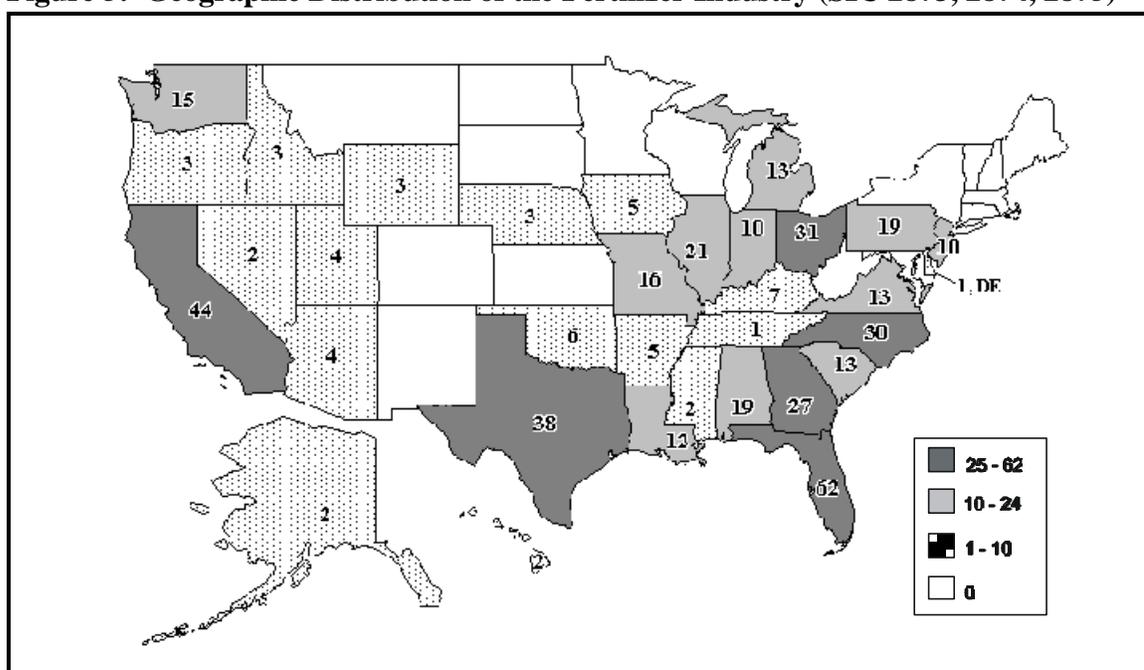
Source: 1992 Census of Manufacturers, Industry Series: Agricultural Chemicals, US Department of Commerce, Bureau of the Census, May 1995.

Note: 1992 Census of Manufacturers data are the most recent available. Changes in the number of facilities, location, and employment figures since 1992 are not reflected in these data.

* United States EPA has identified over 8,600 registered pesticide producing establishments. The SIC code as it is defined by the OMB only includes 263 of those establishments.

Figure 5 shows the United States distribution of fertilizer manufacturing and mixing facilities. The geographic distribution of nitrogenous and phosphatic fertilizer manufacturers is determined by natural resources and demand. Seventy percent of synthetic ammonia plants in the United States are concentrated in Louisiana, Texas, Oklahoma, Iowa, and Nebraska due to abundant natural gas supplies. The majority of nitric acid plants are located in agricultural regions such as the Midwest, South Central, and Gulf States in order to accommodate the high volume of fertilizer usage. Florida has the largest phosphate rock supply in the United States, thus phosphoric acid manufacturing is concentrated primarily in Florida and spreads into the Southeast.

Figure 5: Geographic Distribution of the Fertilizer Industry (SIC 2873, 2874, 2875)



Source: 1992 Census of Manufacturers, Industry Series: Agricultural Chemicals, United States Department of Commerce, Bureau of the Census, May 1995.

Table 7 further divides the geographic distribution of fertilizer manufacturing and mixing facilities. The top states in which the nitrogenous fertilizer, phosphatic fertilizer, and fertilizer mixing industries are concentrated are given along with their respective number of establishments. Florida's supply of phosphate rock causes a concentration of phosphatic and mixed fertilizer facilities, while nitrogenous fertilizer plants are often located near sources of raw materials.

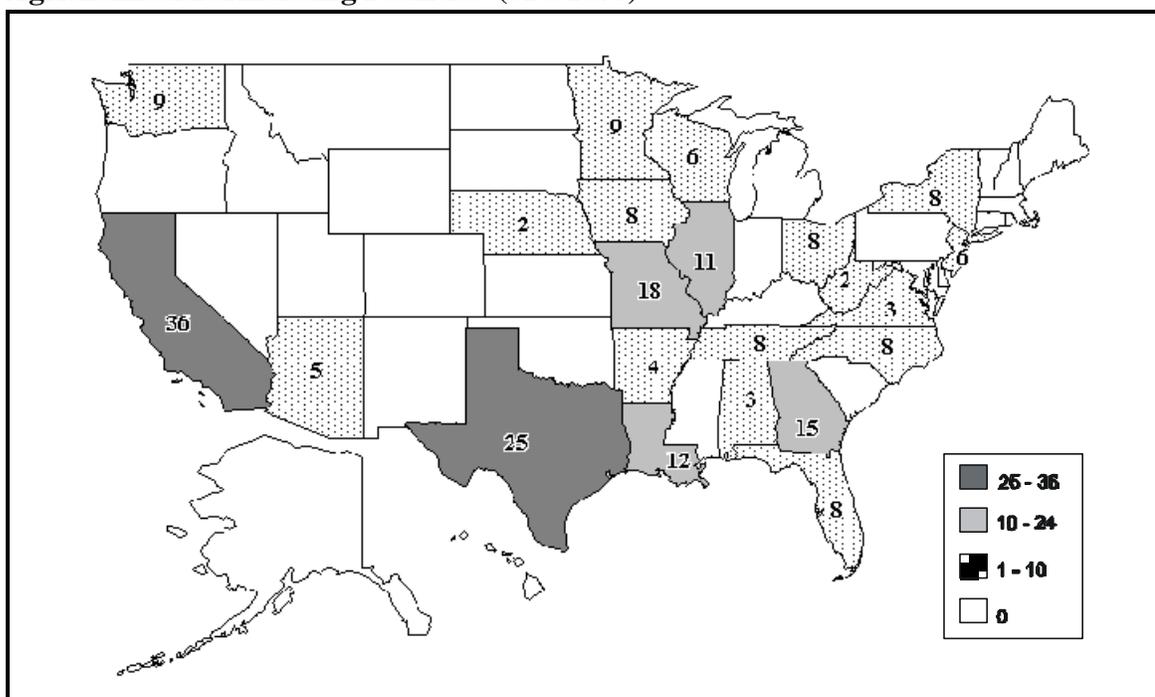
States in which industry is concentrated, based on number of establishments	Nitrogenous Fertilizers (SIC 2873)		Phosphatic Fertilizers (SIC 2874)		Fertilizers, Mixing only (SIC 2875)	
	Top States	Establishments	Top States	Establishments	Top States	Establishments
	California	17	Florida	15	Florida	42
Texas	12	North Carolina	9	Ohio	31	
Louisiana	8			Texas	26	
% of total	24%		32%		25%	

Source: 1992 Census of Manufacturers, Industry Series: Agricultural Chemicals, US Department of Commerce, Bureau of the Census, May 1995.

Note: 1992 Census of Manufacturers data are the most recent available. Changes in the number of facilities, location, and employment figures since 1992 are not reflected in these data.

Figure 6 shows the United States distribution of pesticide formulating and miscellaneous agrichemical formulating facilities. The distribution follows the general distribution of the petrochemical industry (coasts and Great Lakes) which the industry relies on for its raw materials, and the distribution of agricultural production in the United States (Midwest and Great Plains states).

Figure 6: Geographic Distribution of the Pesticide Formulating and Miscellaneous Agrichemical Formulating Facilities (SIC 2879)*



Source: 1992 Census of Manufacturers, Industry Series: Agricultural Chemicals, United States Department of Commerce, Bureau of the Census, May 1995.

* United States EPA has identified over 8,000 establishments that could fall within this SIC code as it is defined by the OMB.

Table 8: Top United States Agricultural Chemical Companies			
Rank	Company	1997 Sales (millions of dollars)	SIC Code(s) Reported
1	IMC Global - Northbrook, IL	2,981	2874, 2875, 2819, 1474, 1475
2	Zeneca Inc. - Wilmington, DE	2,822	2879, 2834, 2899
3	Agrium United States Inc. - Spokane, WA	1,814	2873
4	CF Industries, Inc. - Lake Zurich, IL	1,383	2873, 2874
5	PCS Nitrogen Inc. - Memphis, TN	1,310	2873, 2874
6	Dowelanco (now named Dow AgriSciences) - Indianapolis, IN	1,288	2879
7	The Scotts Company - Marysville, OH	752	2873, 2874, 2879, 0139, 2499, 3524
8	Cargill Fertilizer - Riverview, FL	600	2874
9	ChemFirst Inc. - Jackson, MS	595	2873, 2865, 3567, 3312
10	La Roche Industries Inc. - Atlanta, GA	449	2873, 5191, 2812, 2869, 3291, 3569
<i>Source: Dun & Bradstreet's Million Dollar Directory, 1997</i>			
Note: Not all sales can be attributed to the companies agricultural chemical operations.			

Dun & Bradstreet's *Million Dollar Directory*, compiles financial data on United States companies including those operating within the Fertilizer, Pesticide, and Agricultural Chemical Industry. Dun & Bradstreet ranks United States companies, whether they are a parent company, subsidiary or division, by sales volume within their assigned 4-digit SIC code. Readers should note that: (1) companies are assigned a 4-digit SIC code that resembles their principal industry most closely; and (2) sales figures include total company sales, including subsidiaries and operations (possibly not related to agricultural chemicals). Additional sources of company specific financial information include Standard & Poor's *Stock Report Service*, Ward's *Business Directory of United States Public and Private Companies*, Moody's Manuals, and annual reports.

The Bureau of the Census publishes concentration ratios, which measure the degree of competition in a market. They compute the value of shipments percentage controlled by the top 4, 8, 20, and 50 companies in a given industry. Within the agricultural chemical industry, the phosphatic fertilizer

industry had the highest concentration ratio for the top four companies in 1992, 62 percent. The pesticide and other agricultural chemicals, nitrogenous fertilizers, and fertilizer mixing industries' concentration ratios were 53, 48, and 19 percent respectively.

II.B.3. Economic Trends

The United States is a major producer and exporter of agricultural chemicals. It is the largest producer of phosphatic fertilizers and pesticides and the second largest producer of nitrogenous fertilizers in the world (USDOC, 1998).

Domestic Market Trends

The majority of important crops, such as corn and soybeans, are grown using fertilizers and pesticides. As a result, year-to-year changes in the domestic demand for agrichemicals reflect the level of planted acreage, which in turn is affected by grain prices and weather conditions. Increases in planted acreage of corn, feedgrains and other crops in recent years have resulted in increased demand and production of agrichemicals in the United States. Industry shipments of agricultural chemicals should show modest annual growth through the end of the decade (USDOC, 1998).

The Federal Agricultural Improvement and Reform Act of 1996 could have a major long-term impact on the agricultural chemical industry. This law gives farmers greater flexibility in making planting decisions and allows them to rely more on the marketplace as a guide for crop plantings. The bill eliminates the annual acreage set-aside program, thus potentially boosting the levels of crop acreage (USDOC, 1998).

Agricultural chemical production showed little change between 1995 and 1996. Total production was approximately 103 million pounds each year. However, experts claim that due to lower dosage requirements for pesticides, agrichemical demand is actually higher than it would appear. Pesticides saw a six percent rise in production from 1995 to 1996. Nitrogenous fertilizer production was up approximately seven percent, and phosphate production increased slightly except for its major product, diammonium phosphate. Prices for agricultural chemicals rose three percent from 1995 to 1996, while the number of production workers fell two percent (USDOC, 1998).

International Market Trends

The United States accounts for more than 50 percent of world trade in phosphatic fertilizers, with a two-thirds share of total trade in DAP (diammonium phosphate), the principal phosphatic fertilizer product. Exports generally account for about half of total shipments for the United States phosphatic fertilizer industry, with about half of all exports going to China.

International markets, especially less developed nations in Asia and Latin America, hold greater market potential for the agrichemicals industry as population levels grow, income levels rise, and demands for better standards of living and diets increase the need for grain production. From the current level of about 5.8 billion, the world population is expected to increase by about 80 million each year between 1996 and 2000. Developing nations are becoming more sophisticated in agricultural practices, thus increasing their usage of fertilizers and pesticides to improve production (USDOC, 1998).

The United States has been a net exporter of pesticide chemicals, and this is expected to continue through the turn of the century. Exports of pesticides accounted for about 25 percent of United States pesticide production in 1994, according to The American Crop Protection Association. United States pesticide producers benefit from a highly developed chemical sector and strong demand from developing regions of the world. Nevertheless, export opportunities are being restrained by industry-wide globalization as producers are choosing to site facilities closer to end-use markets. In addition, regulatory reforms in Western Europe, such as the competitive access provider plan, are expected to limit prospects in that region, currently the largest destination for United States produced pesticides (USDOC, 1998).

International competition for the United States phosphatic fertilizer industry generally comes from countries with phosphate rock reserves and capacity to convert rock into phosphate chemicals. Diammonium phosphate imports are expected to account for most of the growth in world trade, thus giving the United States a promising outlook for this product. Morocco possesses at least 50 percent of the world's rock reserves and is the largest phosphate rock exporter. China and Russia are also major phosphate rock and fertilizer producers, with Russia also a leading exporter of phosphate chemicals. In the world pesticide markets, major competitors are companies based in Germany, France, and Switzerland.

The United States is a net importer of nitrogenous fertilizers. Trinidad and Tobago and Canada are the leading United States suppliers of nitrogen due to their low-cost supplies of natural gas.

Agricultural biotechnology is beginning to play a major role in agricultural pest control, spurred on by government pesticide restrictions, increased insect resistance to pesticides, and farmers' demand for productivity gains. Genetically engineered plants will be higher yielding, more resistant to disease and insects, and tolerant to herbicides. A number of companies have received approvals for the use of genetically engineered seeds, including corn and cotton, that are resistant to insects and herbicide tolerant. Commercial usage should increase rapidly over the next few years (USDOC, 1998).

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III. INDUSTRIAL PROCESS DESCRIPTION

This section describes the major industrial processes within the Fertilizer, Pesticide, and Agricultural Chemical Industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of resource materials and contacts that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the by-products produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process. This section also describes the potential fate (via air, water, and soil pathways) of these waste products.

The three most important nutrients for plant growth are nitrogen, phosphorous, and potassium. However, the production of the major potassium fertilizer salts, or potash as they are commonly known, is typically considered an inorganic chemical process (SIC 2819). Therefore, the discussion of fertilizer production in this notebook is restricted to nitrogenous and phosphatic mixtures. The fertilizer, pesticide, and agricultural chemical industry can be divided into Nitrogenous Fertilizers, Phosphatic Fertilizers, Fertilizers (Mixing-only), and the formulating and preparing of pesticides and other agricultural chemicals. A detailed description of the production processes for nitrogenous and phosphatic fertilizers is presented here, along with brief descriptions of the fertilizer mixing and pesticide formulating and preparing industry.

III.A. Nitrogenous Fertilizers

The major nitrogenous fertilizers include synthetic ammonia, ammonium nitrate, and urea. The various industrial processes used to manufacture these products are described, as well as the production process for nitric acid, an important intermediate in nitrogenous fertilizer production.

III.A.1. Synthetic Ammonia

Synthetic ammonia (NH_3) is produced by reacting hydrogen with nitrogen at a molar ratio of three to one. Nitrogen is obtained from the air, which is primarily comprised of nitrogen (78 percent) and oxygen (21 percent) (Lewis, 1993). Hydrogen is obtained from either the catalytic steam reforming of

natural gas (methane) or naphtha, or as the byproduct from the electrolysis of brine at chlorine plants. In the United States, about 98 percent of the hydrogen used to synthesize ammonia is produced by catalytic steam reforming of natural gas, and only 2 percent is obtained from chlorine plants (USEPA, 1993a).

Six process steps are required to produce synthetic ammonia using the catalytic steam reforming method:

- 1) natural gas desulfurization
- 2) catalytic steam reforming
- 3) carbon monoxide shift
- 4) carbon dioxide removal
- 5) methanation
- 6) ammonia synthesis.

The first, third, fourth, and fifth steps remove impurities such as sulfur, CO, CO₂ and water from the feedstock, hydrogen and synthesis gas streams. In the second step, hydrogen is manufactured and mixed with air (nitrogen). The sixth step produces anhydrous ammonia from the synthetic gas. An anhydrous compound is inorganic and does not contain water either adsorbed on its surface or combined as water of crystallization. While almost all ammonia plants use these basic process steps, details such as operating pressures, temperatures, and quantities of feedstock vary from plant to plant. Figure 7 shows a simplified process flow diagram of a typical ammonia plant (USEPA, 1993a).

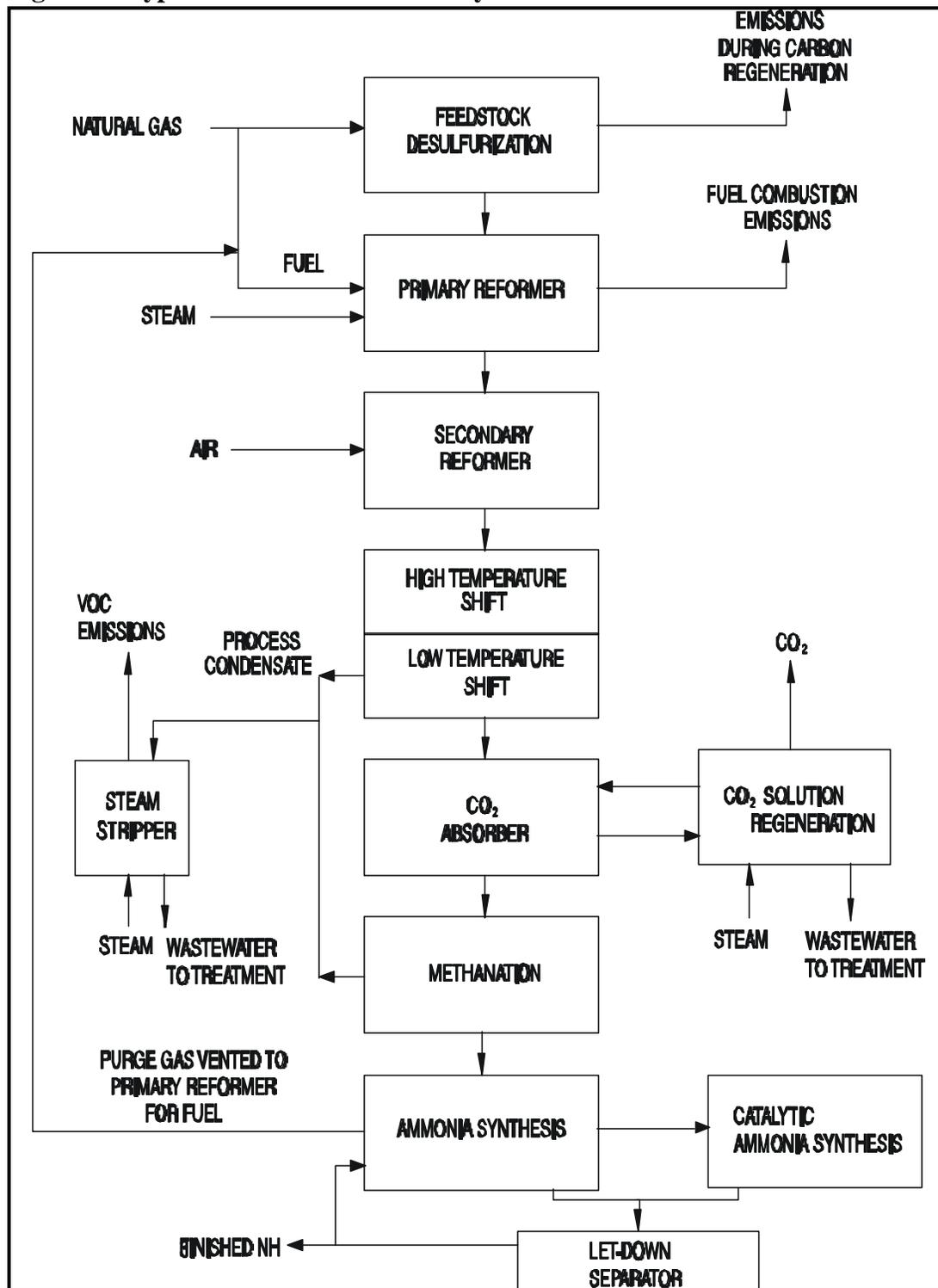
Natural gas desulfurization

In the natural gas desulfurization step, the sulfur content (primarily as H₂S) in natural gas feedstock is reduced to below 280 micrograms per cubic meter to prevent poisoning of the catalyst used in the catalytic steam reforming step. Desulfurization can be accomplished by passing the natural gas through a bed of either activated carbon or zinc oxide. In both systems, the hydrogen sulfide in the gas adsorbs to the surface of the activated carbon or zinc oxide medium and the desulfurized natural gas passes through.

Over 95 percent of the ammonia plants in the United States use activated carbon fortified with metallic oxide additives for feedstock desulfurization. After a certain amount of impurities adsorb to the activated carbon, its effectiveness is reduced and it must be regenerated by passing superheated steam through the carbon bed. The superheated steam strips out the sulfur impurities, is condensed, and sent to the wastewater treatment plant. One disadvantage of the activated carbon system is that some of the heavy hydrocarbons in the natural gas adsorb to the carbon, decreasing its effectiveness and lowering the heating value of the desulfurized gas.

The remaining five percent of plants use zinc oxide for desulfurization. The zinc oxide system is capable of absorbing up to 20 percent sulfur by weight

Figure 7: Typical Process of Ammonia Synthesis



Source: United States EPA, 1993a.

(Hodge, 1994). Zinc oxide is replaced rather than regenerated, which lowers

energy consumption and minimizes impact to the atmosphere. The higher molecular weight hydrocarbons are not removed; therefore, the heating value of the natural gas is not reduced. However, it is impractical and uneconomical to replace the zinc oxide beds so few plants use it (USEPA, 1993a).

Catalytic steam reforming

Next, the desulfurized natural gas is preheated by mixing with superheated steam. The mixture of steam and gas enters the primary reformer tubes which are filled with a nickel-based reforming catalyst, and the tubes are heated by natural gas or oil-fired burners. Approximately 70 percent of the methane (CH₄) is converted to hydrogen (H₂) and carbon dioxide (CO₂), according to the following reaction:



The remainder of the CH₄ is converted to H₂ and CO. This process gas is then sent to the secondary reformer, where it is mixed with compressed hot air at 540°C (1004°F). Sufficient air is added to produce a final synthesis gas having a hydrogen-to-nitrogen mole ratio of three to one. The gas leaving the secondary reformer (primarily hydrogen, nitrogen, CO, CO₂, and H₂O) is then cooled to 360°C (680°F) in a waste heat boiler before being sent to the carbon monoxide shift (USEPA, 1993a).

Carbon monoxide shift

After cooling, the secondary reformer effluent gas enters a high temperature (350-400°C) CO shift converter which converts the CO to CO₂, followed by a low temperature (200-250°C) shift converter which continues to convert CO to CO₂ (Kroschwitz and Howe-Grant, 1992). The high temperature CO shift converter is filled with chromium oxide initiator and iron oxide catalyst. The following reaction takes place (USEPA, 1993a):



The exit gas is then cooled in a heat exchanger before being sent to a low temperature shift converter for ammonia, amines, and methanol where CO continues to be converted to CO₂ by a copper oxide/zinc oxide catalyst (Kent, 1992). In some plants, the gas is first passed through a bed of zinc oxide to remove any residual sulfur contaminants that would poison the low temperature shift catalyst. In other plants, excess low temperature shift catalyst is added to ensure that the unit will operate as expected. Final shift gas from this converter is cooled from 210 to 110°C (410 to 230°F) and unreacted steam is condensed and separated from the gas in a knockout drum. The final shift gas then enters the bottom of the carbon dioxide absorption system. The condensed steam (process condensate) contains ammonium carbonate ((NH₄)₂CO₃ • H₂O) from the high temperature shift converter, methanol (CH₃OH) from the low temperature shift converter, and small amounts of sodium, iron, copper, zinc, aluminum and calcium. Process condensate is sent to the stripper

to remove volatile gases such as ammonia, methanol, and carbon dioxide. Trace metals remaining in the process condensate are typically removed in an ion exchange unit (USEPA, 1993a).

Carbon dioxide removal

In this step, CO₂ in the final shift gas is removed. CO₂ removal can be done by using one of two methods: monoethanolamine (C₂H₄NH₂OH) scrubbing or hot potassium scrubbing. Approximately 80 percent of the ammonia plants use monoethanolamine (MEA) for removing CO₂. In this process, the CO₂ gas is passed upward through an adsorption tower countercurrent to a 15 percent to 30 percent solution of MEA in water fortified with corrosion inhibitors. After absorbing the CO₂, the amine-CO₂ solution is preheated and regenerated in a reactivating tower. The reacting tower removes CO₂ by steam stripping and then by heating. The CO₂ gas (98.5 percent CO₂) is either vented to the atmosphere or used for chemical feedstock in other parts of the plant complex. The regenerated MEA is pumped back to the absorber tower after being cooled in a heat exchanger and solution cooler (USEPA, 1993a).

Methanation

Carbon dioxide absorption is not 100 percent effective in removing CO₂ from the gas stream, and CO₂ can poison the synthesis converter. Therefore, residual CO₂ in the synthesis gas must be removed by catalytic methanation. In a reactor containing a nickel catalyst and at temperatures of 400 to 600°C (752 to 1112°F) and pressures up to 3,000 kPa (435 psia) methanation follows the following reaction steps:



Exit gas from the methanator is almost a pure three to one mole ratio of hydrogen to nitrogen (USEPA, 1993a).

Ammonia Synthesis

In the synthesis step, the hydrogen and nitrogen synthesis gas from the methanator is converted to ammonia.



First, the gas is compressed to pressures ranging from 13,800 to 34,500 kPa (2000 to 5000 psia), mixed with recycled synthesis gas, and cooled to 0°C (32°F). This results in a portion of the gas being converted to ammonia which is condensed and separated from the unconverted synthesis gas in a liquid-vapor separator and sent to a let-down separator. The unconverted synthesis gas is further compressed and heated to 180°C (356°F) before entering a synthesis converter containing an iron oxide catalyst. Ammonia gas exiting the

synthesis converter is condensed and separated, then sent to the let-down separator. A small portion of the overhead gas is purged to prevent the buildup of inert gases such as argon in the circulating gas system. Ammonia in the let-down separator is flashed to atmospheric pressure (100 kPa (14.5 psia)) at -33°C (-27°F) to remove impurities from the make-up gas. The flash vapor is condensed in a let-down chiller where anhydrous ammonia is drawn off and stored at low temperature (USEPA, 1993a).

Storage and Transport

Ammonia is typically stored at ambient pressure and -33°C (-28°F) in large 20,000 ton tanks. Some tanks are built with a double wall to minimize leakage and insulate. If heat leaks into the tank and ammonia is vaporized, the vapors are typically captured, condensed, and returned to the tank. Ammonia is mostly transported by barge to key agricultural areas, but there is also a small system of interstate ammonia pipelines (Kent, 1992).

III.A.2. Nitric Acid

Nitric acid (HNO₃) is produced by two methods. The first method utilizes oxidation, condensation, and absorption of ammonia to produce a “weak” nitric acid. Weak nitric acid has a concentration ranging from 30 to 70 percent nitric acid. The second method combines dehydrating, bleaching, condensing, and absorption to produce “high strength” nitric acid from weak nitric acid. High strength nitric acid generally contains more than 90 percent nitric acid (USEPA, 1993a). The following text discusses each of these processes.

Weak Nitric Acid Production

Nearly all the weak nitric acid produced in the United States is manufactured by the high temperature catalytic oxidation of ammonia as shown schematically in Figure 8. This process typically consists of three steps:

- 1) ammonia oxidation
- 2) nitric oxide oxidation
- 3) absorption.

Each step corresponds to a distinct chemical reaction.

Ammonia Oxidation

During ammonia oxidation, a one to nine ammonia to air mixture is oxidized at a temperature of 750 to 800°C (1380 to 1470°F) as it passes through a catalytic converter, according to the following reaction:



The most commonly used catalyst is made of gauze squares of fine wire constructed of 90 percent platinum and 10 percent rhodium. Under these

conditions the oxidation of ammonia to nitric oxide (NO) proceeds in an exothermic reaction with 93 to 98 percent yield. Higher catalyst temperatures increase reaction selectivity toward nitric oxide (NO) production. Lower catalyst temperatures tend to be more selective toward nitrogen (N₂) and nitrous oxide (N₂O) (USEPA, 1993a). The nitric oxide then passes through a waste heat boiler and a platinum filter in order to recover the precious metal platinum (Kent, 1992).

Nitric Oxide Oxidation

The nitric oxide formed during the ammonia oxidation is further oxidized in another process step. The nitric oxide process stream is passed through a cooler/condenser and cooled to 38°C (100°F) or less at pressures up to 800 kPa (116 psia). The nitric oxide reacts noncatalytically with residual oxygen to form nitrogen dioxide and its liquid dimer, dinitrogen tetroxide:



(A dimer is a small polymer whose molecule is composed of two molecules of the same composition (Lewis, 1993).) This slow, homogeneous reaction is temperature and pressure dependent. Operating at low temperatures and high pressures promotes maximum production of NO₂ within a minimum reaction time (USEPA, 1993a).

Nitrogen dioxide absorption

The final step introduces the gaseous nitrogen dioxide/dimer mixture into an absorption process after being cooled. The mixture is pumped into the bottom of an absorption tower with trays, while liquid dinitrogen tetroxide (N₂O₄) is added at a higher point. Deionized water enters the top of the column. Both liquids flow countercurrent to the dioxide/dimer gas mixture. The exothermic reaction occurs as follows (USEPA, 1993a):



A secondary air stream is introduced into the column to re-oxidize the NO that is formed. This secondary air also removes NO₂ from the product acid. Oxidation of NO to NO₂ takes place in the free space between the trays, while absorption of NO₂ into the water occurs on the trays. An aqueous solution of 55 to 65 percent (typically) nitric acid is withdrawn from the bottom of the tower. The acid concentration can vary from 30 to 70 percent nitric acid depending upon the temperature, pressure, number of absorption stages, and concentration of nitrogen oxides entering the absorber (USEPA, 1993a).

There are two variations of the process described above to produce weak nitric acid: single-stage pressure process and dual-stage pressure process. In the past, nitric acid plants have been operated at a single pressure, ranging from atmospheric pressure to 1400 kPa (14.7 to 203 psia). However, since the oxidation of ammonia is favored by low pressures and the oxidation of

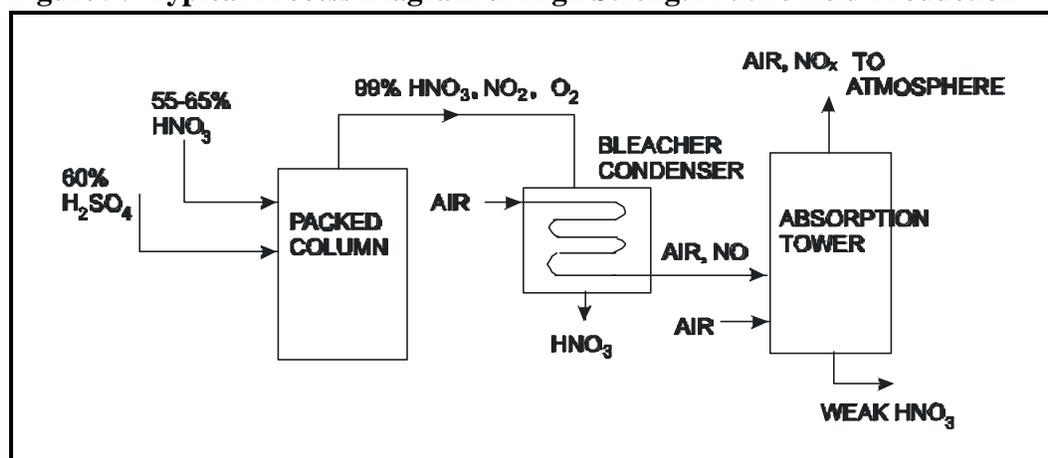
nitric oxide and the absorption of nitrogen dioxide are favored by higher pressures, newer plants tend to operate a dual-stage pressure system, incorporating a compressor between the ammonia oxidizer and the condenser. The oxidation reaction is carried out at pressures from slightly negative to about 400 kPa (58 psia), and the absorption reactions are carried out at 800 to 1,400 kPa (116 to 203 psia) (USEPA, 1993a).

In the dual-stage pressure system, the nitric acid formed in the absorber (bottoms) is usually sent to an external bleacher where air is used to remove (bleach) any dissolved oxides of nitrogen (NO, NO₂, etc.). The bleacher gases are then compressed and again passed through the absorber. The absorber tail gas (distillate) is sent to an entrainment separator for acid mist removal. Next, the tail gas is reheated in the ammonia oxidation heat exchanger to approximately 200°C (392°F). The gas is then passed through catalytic reduction units for NO_x emissions control. The final step expands the gas in the power-recovery turbine. The thermal energy produced in this turbine can be used to drive the compressor.

The nitric acid concentration process consists of feeding strong sulfuric acid and 55 to 65 percent nitric acid into the top of a packed dehydrating column at approximately atmospheric pressure. The acid mixture flows downward and concentrated nitric acid leaves the top of the column as 99 percent vapor, containing a small amount of NO_2 and O_2 resulting from dissociation of nitric acid. The concentrated acid vapor then goes to a bleacher and a countercurrent condenser system to condense strong nitric acid and separate out the oxygen and nitrogen oxide by-products. The bleacher uses air to strip nitrogen oxides out of the nitric acid and the countercurrent condenser system cools the vapor by flowing air through the vapor causing droplets to separate out.

These nitrogen oxide by-products then flow to an absorption column where the nitric oxide mixes with auxiliary air to form NO_2 , which is recovered as weak nitric acid. Inert and unreacted gases are vented to the atmosphere from the top of the absorption column. Emissions from this process are relatively small compared to weak acid production (USEPA, 1993a). Figure 9 illustrates a typical high strength nitric acid production process.

Figure 9: Typical Process Diagram of High Strength Nitric Acid Production



Source: Adapted from United States EPA, 1993a.

III.A.3. Ammonium Nitrate and Urea

The manufacture steps for ammonium nitrate (NH_4NO_2) and urea ($\text{CO}(\text{NH}_2)_2$) are similar. In both cases, several major unit operations are involved, including:

- 1) solution formation
- 2) concentration
- 3) solids formation
- 4) finishing
- 5) screening

- 6) coating
- 7) product bagging and/or bulk shipping.

These operations are shown schematically in Figure 10. Not all steps are always necessary depending on the end product desired. For example, plants producing ammonium nitrate or urea liquid solutions alone use only the solution formation, solution blending and bulk shipping operations. Plants producing a solid product may employ all of the operations.

Solution synthesis

Ammonium nitrate.

Ammonium nitrate plants produce an aqueous ammonium nitrate solution through the reaction of ammonia and nitric acid in a neutralizer where water is evaporated by the heat of the reaction as follows:



The temperature, pressure, and final concentration of the ammonium nitrate are interdependent. Higher temperatures and pressures can be used to produce a higher concentration of ammonium nitrate (Hodge, 1994); however, the temperature of the operation should be below 120°C (250°F) in order to prevent explosions. Up to 99.5 percent of the ammonia and nitric acid is typically converted to ammonium nitrate (Kent, 1992). Ammonium nitrate solution can then be used as an ingredient for nitrogen solution fertilizers or concentrated to a solid form.

Urea.

In the urea solution synthesis operation, ammonia (NH₃) and carbon dioxide (CO₂) are reacted to form ammonium carbamate (NH₂CO₂NH₄) as follows:



Typical operating conditions include temperatures from 180 to 200°C (356 to 392°F), pressures from 14,000 to 25,000 kPa (140 to 250 psia), molar ratios of NH₃ to CO₂ from 3:1 to 4:1, and a retention time of twenty to thirty minutes. The ammonium carbamate is then dehydrated to yield 70 to 77 percent aqueous urea solution. This reaction follows: (USEPA, 1993a)



Urea solution can be used as an ingredient of nitrogen solution fertilizers, or it can be concentrated further to produce solid urea.

Solids Concentration

Ammonium nitrate.

To produce a solid product, the aqueous ammonium nitrate solution is concentrated in an evaporator or concentrator. The resulting liquid “melt” contains about 95 to 99.8 percent ammonium nitrate at approximately 149°C (300°F). This melt is then used to make solid ammonium nitrate products (USEPA, 1993a).

Urea.

The three methods of concentrating the urea solution are vacuum concentration, crystallization, and atmospheric evaporation. The method chosen depends upon the level of biuret ($\text{NH}_2\text{CONHCONH}_2$) impurity allowable in the end product. Biuret can cause mottling in urea solutions, reducing the fertilizers effectiveness in foliar applications (Kent, 1992). Aqueous urea solution decomposes with heat to biuret and ammonia. Therefore, if only a low level of biuret impurity is allowed in the end product, the method with the least heat requirement will be chosen, such as crystallization and vacuum concentration (Kent, 1992). However, the simplest and most common method of solution concentration is atmospheric evaporation.

Solids Formation

Prilling and granulation are the most common processes used to produce solid ammonium nitrate and urea. Prills are round or needle-shaped artificially prepared aggregates of a material. To produce prills, concentrated melt is sprayed into the top of a prill tower. In the tower, melt droplets fall countercurrent to a rising air stream that cools and solidifies the falling droplets into prills. Prill density can be varied by using different concentrations of ammonium nitrate melt. Low density prills, in the range of 1.29 specific gravity, are formed from a 95 to 97.5 percent ammonium nitrate melt, and high density prills, in the range of 1.65 specific gravity, are formed from a 99.5 to 99.8 percent melt. Low density ammonium nitrate prills are used for making blasting agents because they are more porous than high density prills and will absorb oil. Most high density prills are used as fertilizers (USEPA, 1993a).

Granulated ammonium nitrate and urea are produced by spraying a concentrated melt (99.0 to 99.8 percent) onto small seed particles of ammonium nitrate or urea in a long rotating cylindrical drum. As the seed particles rotate in the drum, successive layers of the nitrogenous chemical are added to the particles, forming granules. Pan granulators operate on the same principle as drum granulators, except the solids are formed in a large, rotating circular pan. Pan granulators produce a solid product with physical characteristics similar to those of drum granules (USEPA, 1993a).

Although not widely used, additives such as magnesium nitrate or magnesium oxide may be injected directly into the melt stream. Additives can serve three

purposes: to raise the crystalline transition temperature of the final solid product in order to retain its strength and density; to act as a desiccant, drawing water into the final product to reduce caking; and to allow solidification to occur at a low temperature by reducing the freezing point of molten ammonium nitrate. (Kent, 1992)

Solids Cooling

The temperature of the nitrogenous product exiting the solids formation process is approximately 66 to 124°C (150 to 255°F). To prevent deterioration and agglomeration, the product must be cooled before storage and shipping. Typically, rotary drums or fluidized beds are used to cool granules and prills leaving the solids formation process. Because low density prills have a high moisture content, they require drying in rotary drums or fluidized beds before cooling (USEPA, 1993a).

Solids Screening

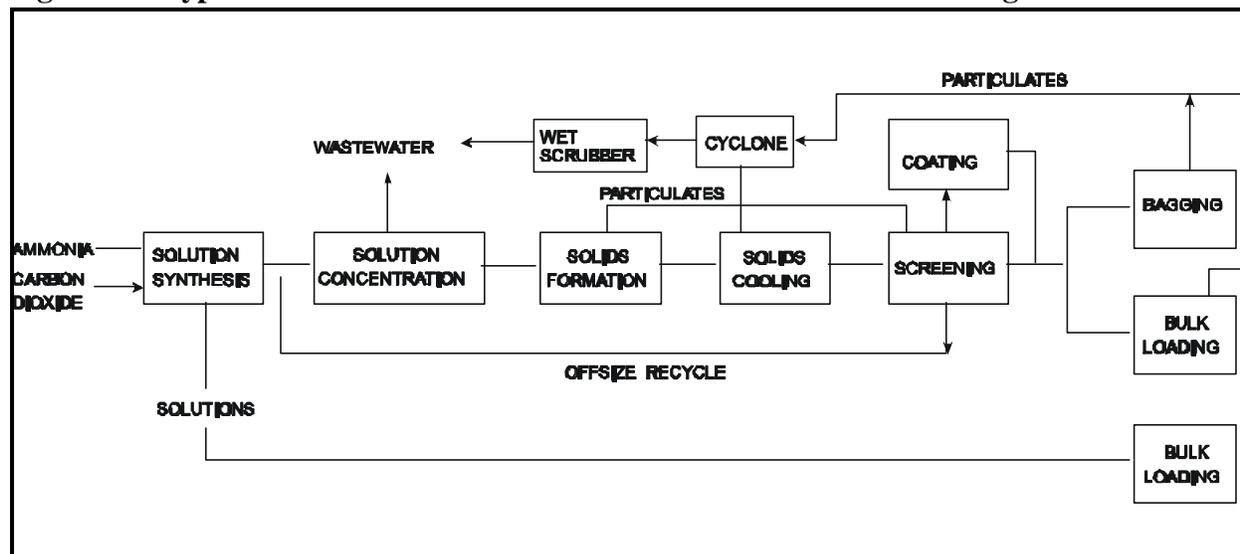
Since the solids are produced in a wide variety of sizes, they must be screened for consistently sized prills or granules. After cooling, off size prills are dissolved and recycled back to the solution concentration process. Granules are screened before cooling. Undersize particles are returned directly to the granulator and oversize granules may be either crushed and returned to the granulator or sent to the solution concentration process (USEPA, 1993a).

Solids Coating

Following screening, products can be coated in a rotary drum to prevent agglomeration during storage and shipment. The most common coating materials are clays and diatomaceous earth. However, the use of additives in the melt before solidification may preclude the use of coatings.

The solid product is stored and shipped in either bulk or bags. The majority of solid product is bulk shipped in trucks, enclosed railroad cars, or barges, and approximately ten percent of solid ammonium nitrate and urea produced in the United States is bagged (USEPA, 1993a).

Figure 10: Typical Process for Ammonium Nitrate and Urea Manufacturing



Source: United States EPA, 1993a.

III.B. Phosphatic Fertilizers

The primary products of the phosphatic fertilizers industry are phosphoric acid, ammonium phosphate, normal superphosphate, and triple superphosphate. Phosphoric acid is sold as is or is used as an intermediate in producing other phosphatic fertilizers. Monoammonium phosphate is favored for its high phosphorous content, while diammonium phosphate is favored for its high nitrogen content. Normal superphosphate has a relatively low concentration of phosphorous, however it is used in mixtures because of its low cost. Triple superphosphate provides a high concentration of phosphorous, more than 40% phosphorous pentoxide. The industrial processes for each of these products are described below.

III.B.1. Phosphoric Acid (Wet Process)

In a wet process phosphoric acid facility (shown schematically in Figure 11), phosphoric acid is produced by reacting sulfuric acid (H_2SO_4) with naturally occurring phosphate rock. The phosphate rock is mined, dried, crushed until 60 to 70 percent of the rock is less than 150 μm in diameter, and then continuously fed into the reactor along with sulfuric acid (UNEP, 1996). The reaction also combines calcium from the phosphate rock with sulfate, forming calcium sulfate ($CaSO_4$), commonly referred to as gypsum. Gypsum is separated from the reaction solution by filtration.

Facilities in the United States generally use a dihydrate process that produces gypsum in the form of calcium sulfate with two molecules of water ($CaSO_4 \cdot 2H_2O$ or calcium sulfate dihydrate). Japanese phosphoric acid facilities use

a hemihydrate process which produces calcium sulfate with a half molecule of water ($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$). This one-step hemihydrate process has the advantage of producing wet process phosphoric acid with a higher phosphate pentoxide (P_2O_5) concentration and less impurities than the dihydrate process. Due to these advantages, some United States companies have recently converted to the hemihydrate process. However, since most wet process phosphoric acid is still produced by the dihydrate process, the hemihydrate process will not be discussed in detail here.

A simplified reaction for the dihydrate process is as follows:



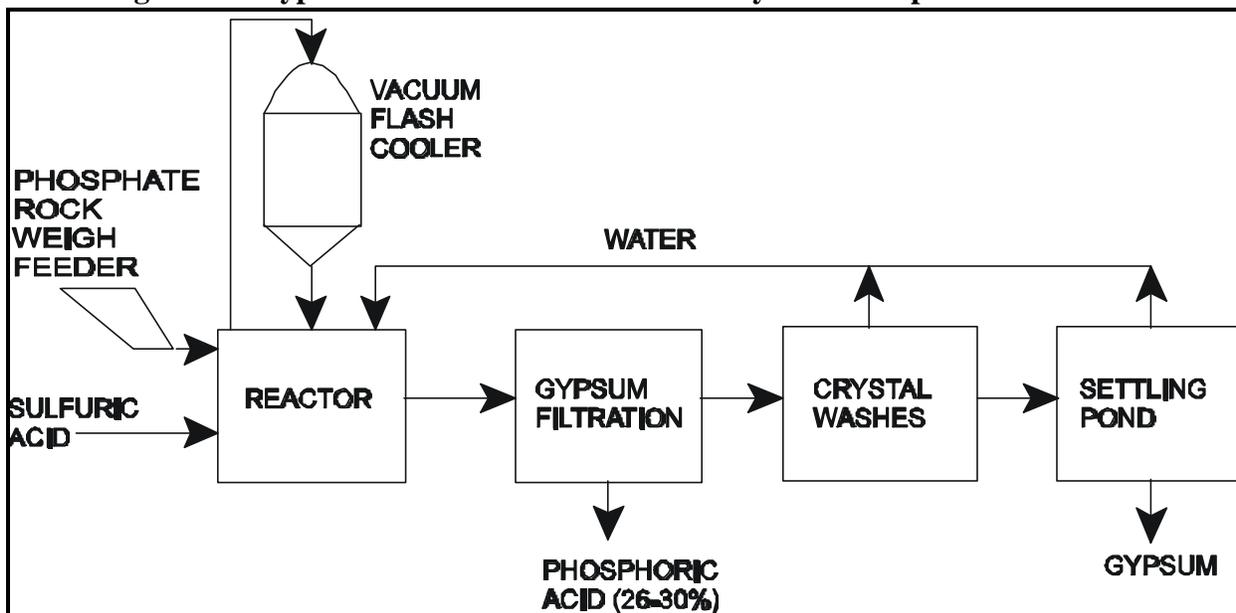
To make the strongest phosphoric acid possible and to decrease evaporation costs, a highly concentrated 93 percent sulfuric acid is normally used. Because the proper ratio of acid to rock in the reactor is critical, precise automatic process control equipment is employed in the regulation of these two feed streams (USEPA, 1993a).

During the reaction, gypsum crystals are precipitated and separated from the acid by filtration. The separated crystals must be washed thoroughly to yield at least a 99 percent recovery of the filtered phosphoric acid. After washing, the slurried gypsum is pumped into a gypsum settling pond for storage. Water is siphoned off and recycled through a surge cooling pond to the phosphoric acid process. Depending on a variety of factors, such as average ambient temperature and annual rainfall, settling and cooling ponds may require between 0.25 and 1.0 acre for each ton of daily P_2O_5 capacity (TFI, 1999).

Considerable heat is generated in the reactor when the sulfuric acid and phosphate rock react. In older plants, this heat was removed by blowing air over the hot slurry surface. Modern plants vacuum flash cool a portion of the slurry, and then recycle it back into the reactor.

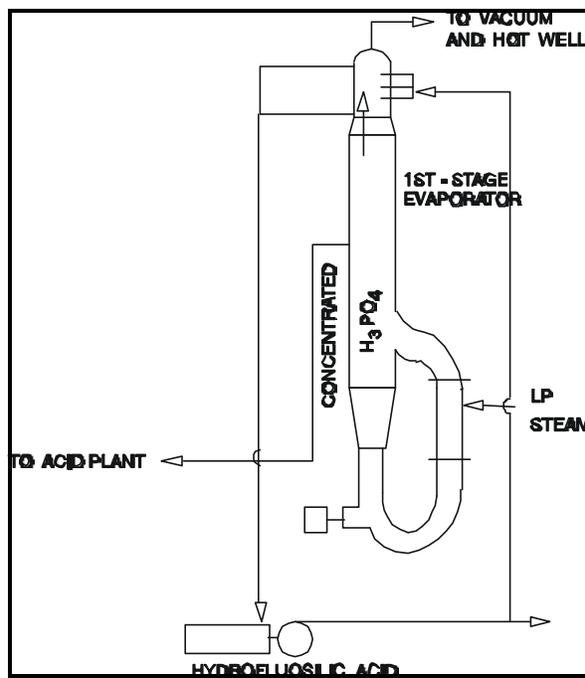
Wet process phosphoric acid normally contains 26 to 30 percent P_2O_5 . In most cases, the acid must be further concentrated to meet phosphate feed material specifications for fertilizer production. Depending on the types of fertilizer to be produced, phosphoric acid is usually concentrated to 40 to 55 percent P_2O_5 by using two or three vacuum evaporators (USEPA, 1993a). These evaporators operate with a forced circulation and generate a vacuum through vacuum pumps, steam ejectors, or an entraining condenser downstream of the evaporator. Figure 12 illustrates a vacuum evaporator.

Figure 11: Typical Process of a Wet Process Dihydrate Phosphoric Acid Plant



Source: Adapted from United States EPA, 1993a.

Figure 12: Typical Vacuum Evaporator Process



Source: United States EPA, 1993a

III.B.2. Ammonium Phosphate

Diammonium phosphate (DAP) and monoammonium phosphate are the major types of ammonium phosphatic fertilizer. Ammonium phosphates are produced by reacting phosphoric acid with ammonia. The ammonium phosphate liquid slurry produced is then converted to solid granules. Approximately 95 percent of ammoniation-granulation plants in the United States use a rotary drum mixer developed and patented by the Tennessee Valley Authority (TVA).

In the TVA DAP process, phosphoric acid is mixed in an acid surge tank with 93 percent sulfuric acid (H_2SO_4) and recycled acid from wet scrubbers. The mixed acids are then partially neutralized with liquid or gaseous anhydrous ammonia in a brick-lined acid reactor. All of the phosphoric acid and approximately 70 percent of the ammonia needed to complete the reaction are introduced into this vessel. A slurry of ammonium phosphate and 22 percent water are produced and sent through steam-traced lines to the ammoniator-granulator.

Slurry from the reactor is distributed in the rotary drum granulator, and the remaining ammonia (approximately 30 percent) is sparged under the slurry. The basic rotary drum granulator consists of an open-ended, slightly inclined rotary cylinder, with retaining rings at each end and a scraper or cutter mounted inside the drum shell. A rolling bed of dry material is maintained in the unit while the slurry is introduced through distributor pipes set lengthwise in the drum. Gravity forces the slurry to travel through the turning granulator to the lower end. Moist DAP granules are then discharged into a rotary dryer, where excess water is evaporated and the chemical reaction is accelerated to completion by the dryer heat. Dried granules are cooled and then sized on vibrating screens. The product ranges in granule diameter from one to four millimeters (mm). The oversized granules are crushed, mixed with the undersized, and recycled back to the ammoniator-granulator. Product-size DAP granules are allowed to cool, screened, bagged, and shipped. Before being exhausted to the atmosphere, particulate and ammonia rich off-gases from the granulator, cooler, and screening operations pass through cyclones and wet scrubbers (USEPA, 1993a).

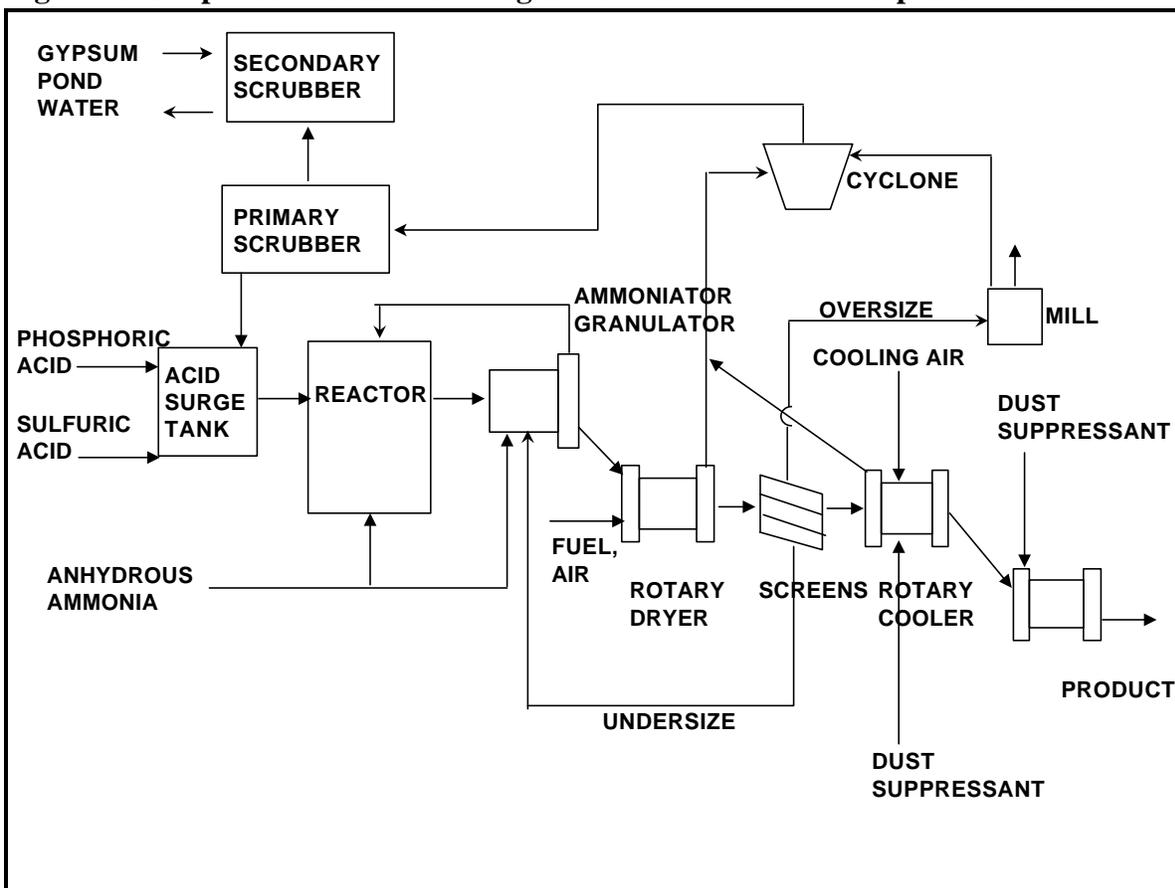
TVA developed two minor modifications in their DAP process to produce Monoammonium Phosphate (MAP). In one, the phosphoric acid is ammoniated to an ammonia to phosphoric acid ratio of only 0.6 in the preneutralizer and then 1.0 in the granulator. This compares to a ratio of about 1.4 for DAP. With the second modification, the ammonium to phosphoric acid ratio is brought to 1.4 in the preneutralizer, then additional phosphoric acid is added in the granulator to bring the ratio back to 1.0. The second method is preferred by industry because higher temperatures may be used to dry the MAP, increasing production rates (Kent, 1992).

A schematic diagram of the ammonium phosphate process flow diagram is

shown in Figure 13.

Source: U.S.EPA, 1993a and TFI, 1999

Figure 13: Simplified Process Flow Diagram of Diammonium Phosphate Production



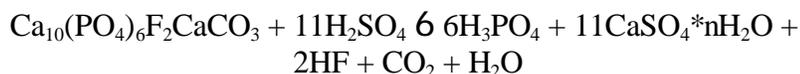
III.B.3. Normal Superphosphate

Normal superphosphates (NSP) are prepared by reacting ground phosphate rock with 65 to 75 percent sulfuric acid to produce a solid fertilizer material. NSP is most often used as a high-phosphate additive in the production of granular fertilizers. It can also be granulated for sale as granulated superphosphate or granular mixed fertilizer.

There are two primary types of sulfuric acid used in superphosphate manufacture: virgin and spent acid. Virgin acid is produced from elemental sulfur, pyrites, and industrial gases and is relatively pure. Spent acid is a recycled waste product from various industries that use large quantities of sulfuric acid. Problems encountered with using spent acid include unusual

color, unfamiliar odor, and toxicity. An important factor in the production of normal superphosphates is the amount of iron and aluminum in the phosphate rock. Aluminum (as Al_2O_3) and iron (as Fe_2O_3) above five percent imparts an extreme stickiness to the superphosphate and makes it difficult to handle (USEPA, 1993a).

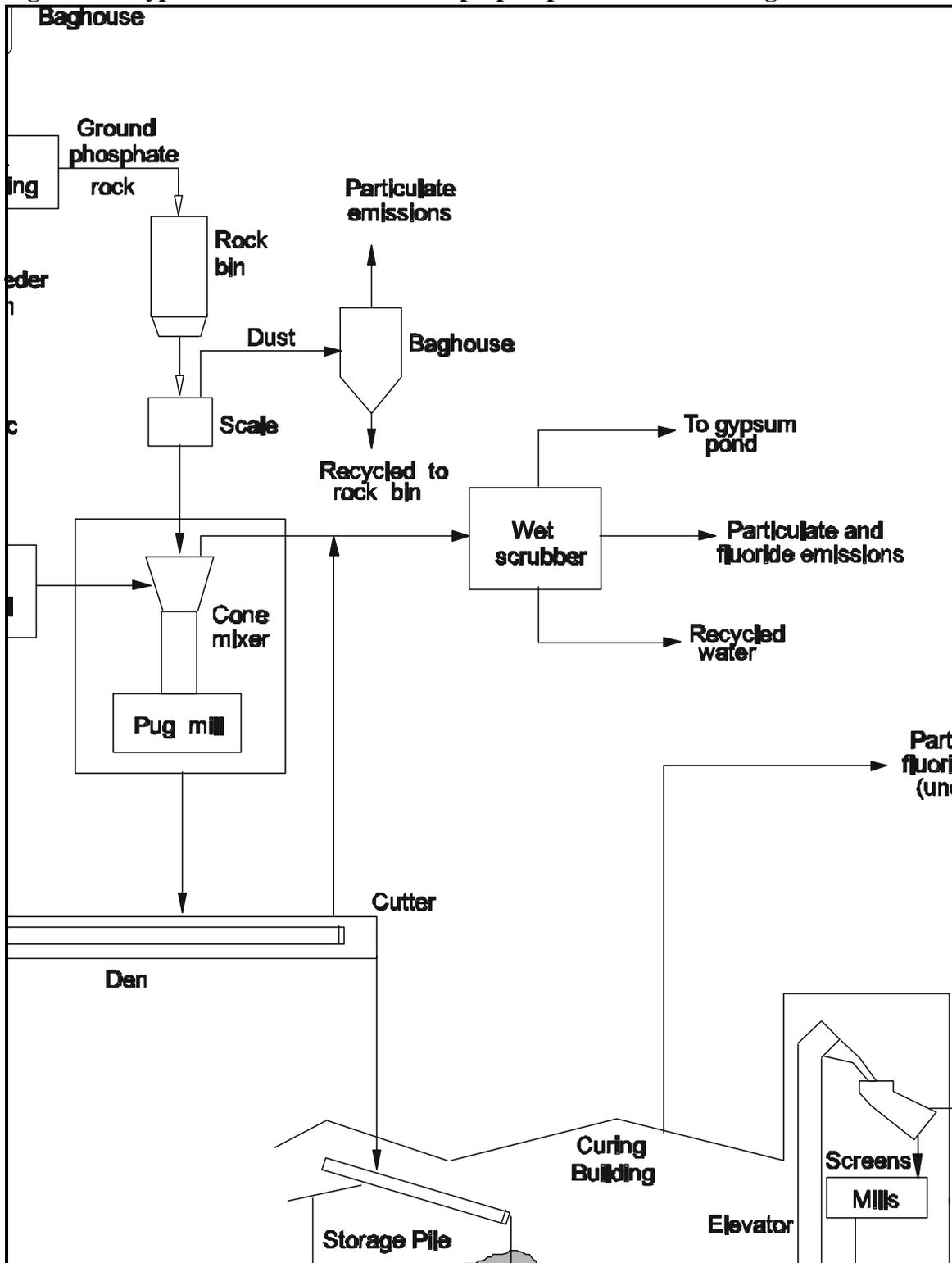
A generalized process diagram of normal superphosphate production is shown in Figure 14. Ground phosphate rock is weighed and mixed with sulfuric acid (H_2SO_4) and held in an enclosed area for about 30 minutes until the reaction is partially completed. The mixing may be done in a cone mixer, which relies on an inputted swirling motion of the acid to mix the rock and acid, a pug mill, which operates with one or two mixing shafts, or a pan mixer, which agitates the solution. The reaction is (AWMA, 1992):



The mixture is then transferred, using an enclosed conveyer known as the den, through the cutter which breaks up clumps, and finally to a storage pile for curing. Off-gases from the reactor are typically treated in a wet scrubber. Particulates throughout the process are controlled with cyclones and baghouses (USEPA, 1993a).

To produce granulated normal superphosphate, cured superphosphate is fed through a clod breaker and sent to a rotary drum granulator where steam, water, and acid may be added to aid in granulation. Material is processed through a rotary drum granulator, a rotary dryer, and a rotary cooler, and is then screened to specification similar to the process used for ammonium nitrate and urea. Finally, it is stored in bagged or bulk form prior to being sold (USEPA, 1993a).

Figure 14: Typical Process for Normal Superphosphate Manufacturing

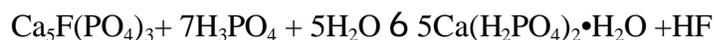


Source: United States EPA, 1993a.

III.B.4. Triple Superphosphate

Triple superphosphate provides a high concentration of phosphorous. Two processes have been used to produce triple superphosphate: run-of-the-pile (ROP-TSP) and granular (GTSP). GTSP yields larger, more uniform particles with improved storage and handling properties than ROP-TSP. At this time, no facilities in the United States are producing ROP-TSP, so only the GTSP process is described here.

Most GTSP material is made with the Dorr-Oliver slurry granulation process, illustrated in Figure 15. This process is similar to that for normal superphosphates with the major exception being that phosphoric acid is used instead of sulfuric acid. In this process, ground phosphate rock or limestone is reacted with phosphoric acid in one or two reactors in series (USEPA, 1993a). The reaction is:



(Hodge, 1994) The phosphoric acid used in this process has a relatively low concentration (40 percent P_2O_5). The lower strength acid maintains the slurry in a fluid state during a mixing period of one to two hours. A small sidestream of slurry is continuously removed and distributed onto dried, recycled fines in a granulator, where it coats the granule surfaces and builds up its size.

Granules are then dried in a rotary dryer, elevated and passed through screens to eliminate oversize and undersize granules. Oversize granules are crushed and sent back to the first screen, while undersize ones are sent into the emission control systems. The granules within the size range of the product are then cooled and stored in a curing pile where the reaction is completed. Particulates from the rock handling, drying, screening, cooling, and storing processes are typically controlled with cyclones and baghouses and off-gases from the reactor, granulator, and cyclones and baghouses are typically treated with wet scrubbers (USEPA, 1993a).

III.C. Fertilizer Mixing

A significant part of the fertilizer industry only purchases fertilizer materials in bulk from fertilizer manufacturing facilities and mixes them to sell as a fertilizer formulation. Fertilizer mixing facilities use many different materials in their blends. The most common granular fertilizer materials are listed in Table 9.

Table 9: Fertilizer Materials Used in Bulk Blends		
	Typical Grade N-P ₂ O ₅ -K ₂ O	Percent of fertilizer plants using this material
Ammonium nitrate	31-0-0	41%
Urea	46-0-0	66%
Ammonium sulfate	21-0-0	22%
Diammonium phosphate (DAP)	18-46-0	95%
Monoammonium phosphate (MAP)	11-52-0	11%
Triple Superphosphate	0-46-0	78%
Normal superphosphate	0-20-0	4%
Potassium chloride	0-0-60	94%

Source: "Retail Marketing of Fertilizers in the United States," by Hargett, Norman and Ralph Pay, 1980.

DAP is favored for fertilizer mixing because of its ease in storage and handling, convenient low nitrogen and high phosphorous content, and compatibility with almost any other material. Granular triple superphosphate is also very popular, but is incompatible with urea, a common nitrogen source. Therefore, TSP is commonly used in no-nitrogen blends necessary for legumes. Ammonium sulfate has the lowest nitrogen content of the major nitrogen sources, however its production cost is quite low. Potassium chloride is the only major potassium source used in fertilizer blending. Additional materials may also be added to the blends, such as micronutrients and pesticides (Nielson, 1987).

Inert ingredients may also be added to fertilizer mixtures to improve the consistency or ease of application. Inert ingredients include sands, clays, and water.

Fertilizer mixing plants consist of five primary phases:

1. mixing and storing
2. moving materials to mixers
3. proportioning of materials
4. mixing, and
5. moving the finished blend to holding bins or transport containers

Fertilizer materials may be mixed as bulk blends or formed into granulations by a variety of processes. Bulk blending is a dry process, where different fertilizers are combined. Materials are typically received by rail cars and transferred through elevators to storage areas. Front-end loaders then carry the materials to weighing hoppers which feed into the mixers. There are two types of mixers most commonly used: the horizontal axis rotary drum mixer and the inclined axis rotary drum mixer. The inclined axis mixer is similar to a cement mixer in design and appearance. Ribbon-type bulk-blend mixers are also used in some plants. A ribbon-type mixer has an axial shaft with mixing spokes radiating out of the shaft in a configuration which forces the blend to flow in a ribbon-like pattern through the mixture (Nielson, 1987).

After preparation and initial bulk blending of materials, granulation may be employed in order to form larger fertilizer particles with multi-nutrient compositions. Granulation of mixed fertilizers may be accomplished by steam granulation, slurry granulation, melt, or compaction granulation.

Steam granulation is primarily used in Europe and Australia. The process results in little chemical reaction in order to maintain the P_2O_5 content of the fertilizer. Plasticity and agglomeration of the fertilizer materials is promoted by the injection of steam into rotating pans, rotary drums, or pug mills. The particles are then dried with heated air in a rotary drum dryer and cooled in a rotary drum cooler. In some cases, particles may be coated with chalk or clay to prevent caking (Hoffmeister, 1993).

Slurry granulation is more commonly used in the United States. The process involves a chemical reaction of the feed ingredients. In slurry granulation, one of the feed ingredients is prepared as a slurry and reacted with the others in a preneutralizer. The slurry is then fed to a granulator such as the ammoniator-granulator developed by the TVA. Fertilizer producers in the United States found that higher concentrations of acid could be fed to this preneutralizer-granulator process than to a granulator alone, thus increasing the grades of fertilizers and making the TVA process popular in the United States (Hoffmeister, 1993).

Another granulation process similar to slurry granulation is melt granulation. The slurry feed is replaced by a hot, concentrated, almost anhydrous melt of feed fertilizer, typically ammonium phosphate, prepared in a pipe reactor. The hot melt provides the plasticity necessary for granulation. The granules cool first in the granulator and then in the cooler, eliminating the need for a dryer.

Compaction granulation is based on the fact that most materials are semiplastic and when subjected to high pressures, the materials will compact, deform, and it is possible to roll them out into flat, stable sheets. These sheets are then cracked, forming granule-size chips which are most stable and less prone to caking than other granulations. This process has been successful for many fertilizer mixtures, particularly those including potassium chloride and ammonium phosphates and superphosphates. Ammonium sulfate, however, has limited crystal plasticity, making it unsuitable for compaction granulation (Hoffmeister, 1993).

The mixtures are then typically bagged in woven polypropylene bags for strength and resistance, with liner bags to prevent leaks. The bags are either clamped, tied, heat sealed, or sewn, sewing being the cheapest and most common method (Nielson, 1987).

III.D. Pesticide Formulating Processes

Pesticide formulation involves the process of mixing, blending, or diluting one or more pesticide active ingredients (AIs) and inert ingredients to obtain a product used for additional processing or an end-use (retail) product. Formulation does not involve an intended chemical reaction (i.e., chemical synthesis). AIs are produced at separate facilities not included in this notebook. Pesticide formulations take many forms: water-based liquid; organic solvent-based liquid; dry products in granular, powder, and solid forms; pressurized gases; and aerosols. The formulations can be in a concentrated form requiring dilution before application, or they can be ready to apply. The packaging of the formulated pesticide product depends on the type of formulation. Liquids generally are packaged into jugs, cans, or drums; dry formulations generally are packaged into bags, boxes, drums, or jugs; pressurized gases are packaged into cylinders; and aerosols are packaged into aerosol cans.

Formulating, packaging, and repackaging is performed in a variety of ways, ranging from very sophisticated and automated formulating and packaging lines to completely manual lines. Descriptions of liquid formulating and packaging, dry formulating and packaging, aerosol packaging, pressurized gas formulating and packaging, and repackaging operations are provided below.

III.D.1. Liquid Formulating and Packaging

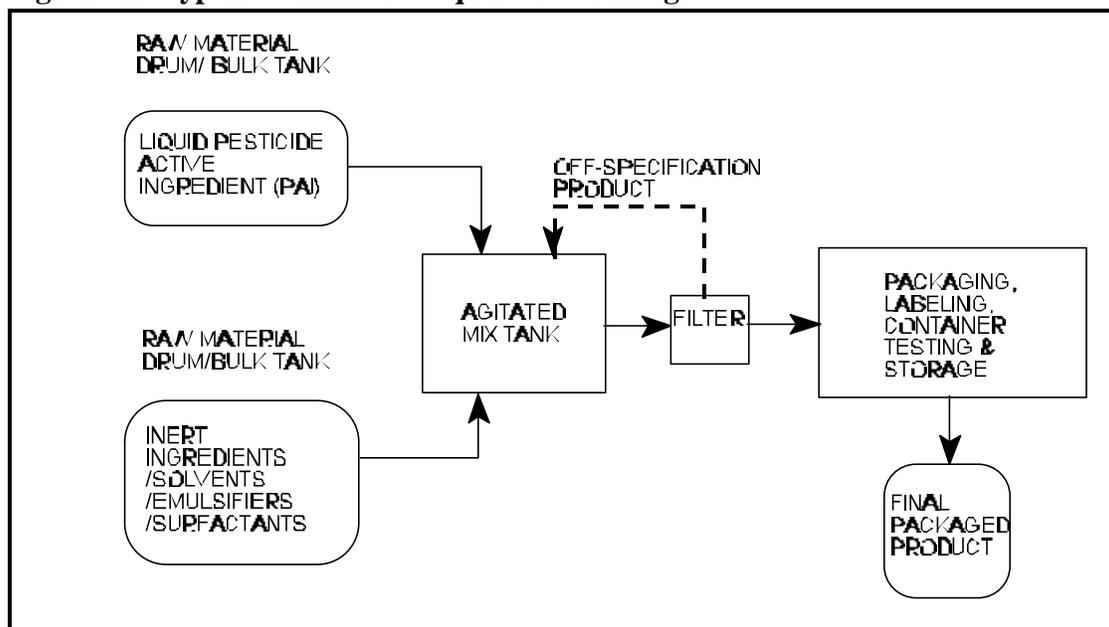
Liquid formulations contain mixtures of several raw materials, including AIs, inert ingredients such as base solvents, emulsifiers, or surfactants. The solvent must be able to dissolve the AIs and other ingredients. It may be water or an organic chemical, such as isopropyl alcohol or petroleum distillate. In some cases, the formulation is an emulsion and contains both water and an organic solvent. Solid materials, such as powders or granules, may also be used as part of a liquid formulation by dissolving or emulsifying the dry materials to form a liquid or suspension. The formulated product may be in a concentrated form requiring dilution before application, or may be ready to apply.

Typical liquid formulating lines consist of storage tanks or containers to hold active and inert raw materials and a mixing tank for formulating the pesticide product. A storage tank may also be used on the formulating line to hold the formulated pesticide product, prior to a packaging step. Facilities may receive their raw materials in bulk and store them in bulk storage tanks, or they may receive the raw materials in smaller quantities, such as 55-gallon drums, 50-pound bags, or 250-gallon minibulk refillable containers or “totes.” These raw materials are either piped to the formulation vessel from bulk storage tanks or added directly to the vessel from drums, bags, or minibulks. Typically, water or the base solvent is added to the formulation vessel in bulk quantities (USEPA, 1996). A typical liquid formulating line is shown in Figure 16.

The formulating line may also include piping and pumps for moving the raw material from the storage tanks to the mixing tank, and for moving formulated pesticide product to the packaging line. Other items that may be part of the line are premixing tanks, stirrers, heaters, bottle washers, and air pollution control equipment. Some lines may also have refrigeration units for formulation and storage equipment, scales, and other equipment.

Many liquid formulations are packaged by simply transferring the final product into containers. Small quantities of product are often manually packaged by gravity feeding the product directly from the formulation tank into the product container. For larger quantities, the process is often automated. Formulated product is transferred to the packaging line through pipes or hoses, or is received from a separate formulating facility and placed in a filler tank. A conveyor belt is used to carry product containers, such as jugs, bottles, cans, or drums, through the filling unit, where nozzles dispense the appropriate volume of product. The belt then carries the containers to a capper, which may be automated or manual, and to a labeling unit. Finally, the containers are packed into shipping cases (USEPA, 1996).

Figure 16: Typical Process for Liquid Formulating



Source: United States EPA, 1996

III.D.2. Dry Formulating and Packaging

Dry formulations also contain active and inert ingredients. The final product may be in many different forms, such as powders, dusts, granules, blocks, solid objects impregnated with pesticide (e.g., flea collars), pesticides formed into a solid shape (e.g., pressed tablets), microencapsulated dusts or granules (AI coated with a polymeric membrane to prevent premature degradation), or encapsulated water soluble packaging. They are formulated in various ways, including:

- C mixing powdered or granular AIs with dry inert carriers;
- C spraying or mixing a liquid active ingredient onto a dry carrier;
- C soaking or using pressure and heat to force active ingredients into a solid matrix;
- C mixing active ingredients with a monomer and allowing the mixture to polymerize into a solid; and
- C drying or hardening an active ingredient solution into a solid form.

These dry pesticide products may be designed to be applied in solid form or dissolved or emulsified in water or solvent prior to application (USEPA, 1996).

Because there are many types of dry pesticide products, dry pesticide formulating lines can vary considerably. In general, though, dry formulating

lines have tanks or containers to hold the active ingredients and inert raw materials, and may include mixing tanks, ribbon blenders, extruding equipment, high pressure and temperature tanks for impregnating solids with active ingredient, vacuums or other types of drying equipment, tanks or bins for storage of the formulated pesticide product, pelletizers, presses, milling equipment, sieves, and sifters (USEPA, 1996).

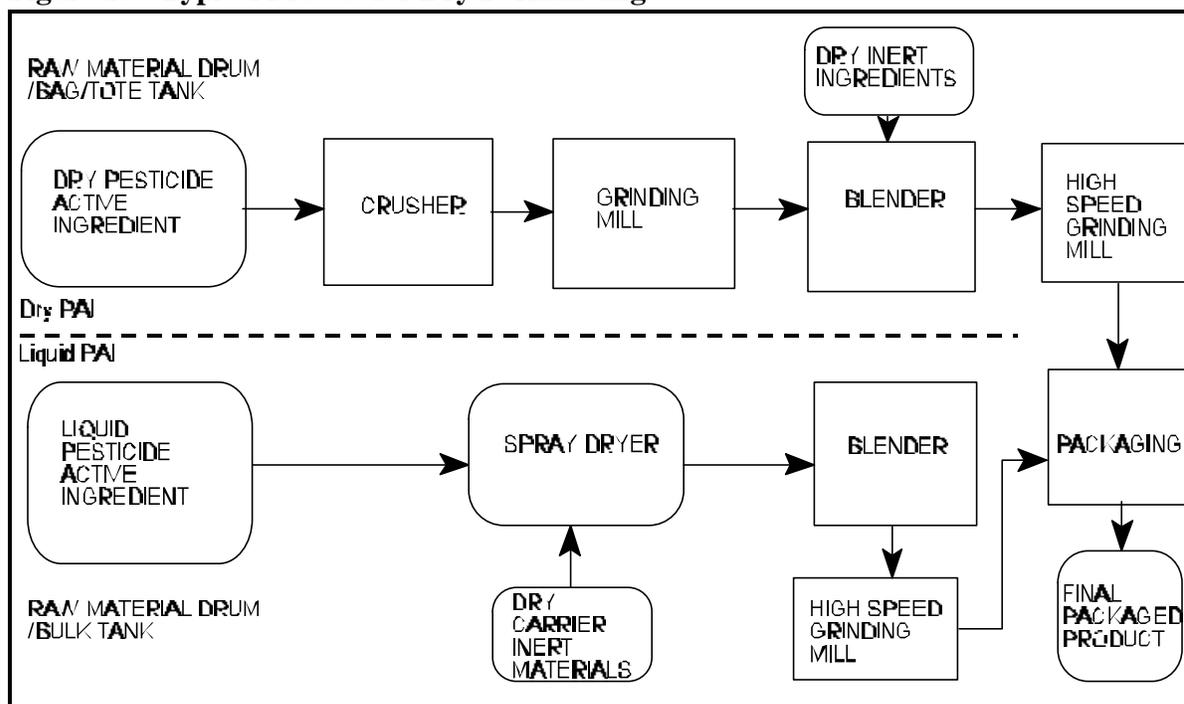
Raw materials for dry pesticide products may be liquid or solid. Liquid raw materials may be stored in rail tank cars, tank trucks, minibulks, drums, or bottles. Dry raw materials may be stored in silos, rail cars, tank trucks, minibulks, metal drums, fiber drums, bags, or boxes. Liquid raw materials may be pumped, poured or sprayed into formulation vessels, while dry raw materials are frequently transferred to formulation equipment by screw conveyors (consisting of a helix mounted on a shaft and turning in a trough), elevators, or by pouring.

Dry formulating lines may also include piping and pumps to move raw materials from storage tanks to the formulation equipment, and to move formulated pesticide product to the packaging equipment. Other items that may be included in the dry pesticide product line are premixing tanks, tanks for storing formulated product prior to packaging, stirrers, heaters, refrigeration units on formulation and storage equipment, scales, and air pollution control equipment (e.g., cyclones, filters, or baghouses) (USEPA, 1996).

Dry pesticide products may be packaged into rail tank cars, tank trucks, totes, and minibulks, but are typically packaged into bags, boxes, and drums. As with many liquid formulations, dry formulations are packaged by simply transferring the final product into boxes, drums, jugs, or bags. Small quantities or bags are typically packaged manually using a gravity feed from the formulating unit into the containers or bags. Larger quantities may be packaged on an automated line, similar to liquid packaging lines.

Figure 17 illustrates a dry pesticide formulation line.

Figure 17: Typical Process for Dry Formulating



Source: United States EPA, 1996

III.D.3. Aerosol Packaging

Some pesticide products (typically water-based or solvent-based liquids) are packaged as aerosols, which can be applied to surfaces or dispersed in the air. The product is placed in spray cans that are put under pressure and a propellant is added, which forces the product out of the can in an aerosol spray. An aerosol packaging line typically includes a filler, a capper, a propellant injector, and a United States Department of Transportation (DOT) test bath. In the filler, formulated pesticide product is dispensed into empty aerosol cans, in much the same way as the liquid packaging lines fill containers. The cans are then sent to the capper, where a cap with a nozzle is placed on the can. The can enters a separate room, where the propellant is injected into the can, a vacuum is pulled, and the cap is crimped to make the can airtight. In order to comply with DOT regulations on the transport of pressurized containers, each can must then be tested for leaks and rupturing in a DOT test bath. Test baths indicate leaks by the appearance of bubbles at the point of leakage on the cylinder. The aerosol packaging line may also include a can washer to remove residue from can exteriors prior to entering the test bath (to reduce contaminant buildup in the bath), a dryer to dry can exteriors, and machinery to package aerosol cans into boxes for shipment (USEPA, 1996).

III.D.4. Pressurized Gas Formulating and Packaging

Some pesticide products are formulated and packaged as pressurized gases, primarily for the purpose of soil fumigation. Soil fumigation is used where the nematodic and fungal populations in soil prohibit successful seed planting. Volatile general toxicants, such as low molecular weight halogenated compounds, are typically injected into the soil before planting, but are also occasionally used once plants have reached maturity (Kent, 1992).

The active and inert ingredients are received as liquid, pressurized liquids, or gases, and are stored in tanks, tank trucks, rail cars, or minibulk storage containers. Liquid ingredients are placed in a holding tank prior to formulation. Formulating and packaging operations for these products usually occurs in one step in a closed-loop system. The ingredients are metered by weight through pressurized transfer lines into DOT-approved steel application cylinders. Other equipment that may be included in a pressurized gas line include pump and piping, and heating and refrigerating units to maintain gas pressures and temperatures in storage (USEPA, 1996).

The cylinders may be refilled at a later date, after they have been tested to ensure that they are still capable of containing pressurized fluids. DOT requires hydrostatic pressure testing, as well as visual examination of the cylinder (USEPA, 1996).

III.D.5. Repackaging

Repackaging operations are similar to packaging operations, except the “raw material” is an already formulated product that has been packaged for sale. Repackagers often purchase formulated pesticide products, transfer the product to new containers with customer-specific labeling, and sell them to distributors (USEPA, 1996).

A separate type of repackaging, called refilling, is usually performed by agrichemical facilities that transfer pesticide products from bulk storage tanks into minibulks. These refillable containers are typically constructed of plastic and typically have capacities ranging from 100 to 500 gallons. Minibulks may be owned by the refilling establishment, the pesticide registrant, or by the end user. Production lines usually consist of a bulk storage tank, a minibulk tank into which the product is repackaged, and any interconnecting hoses or piping. The bulk storage tanks may be dedicated by product and clustered together in a diked area. The products are dispensed to the minibulks by the use of manual system or a computer-regulated system of pumps and meters (USEPA, 1996).

III.E. Raw Material Inputs and Pollution Outputs

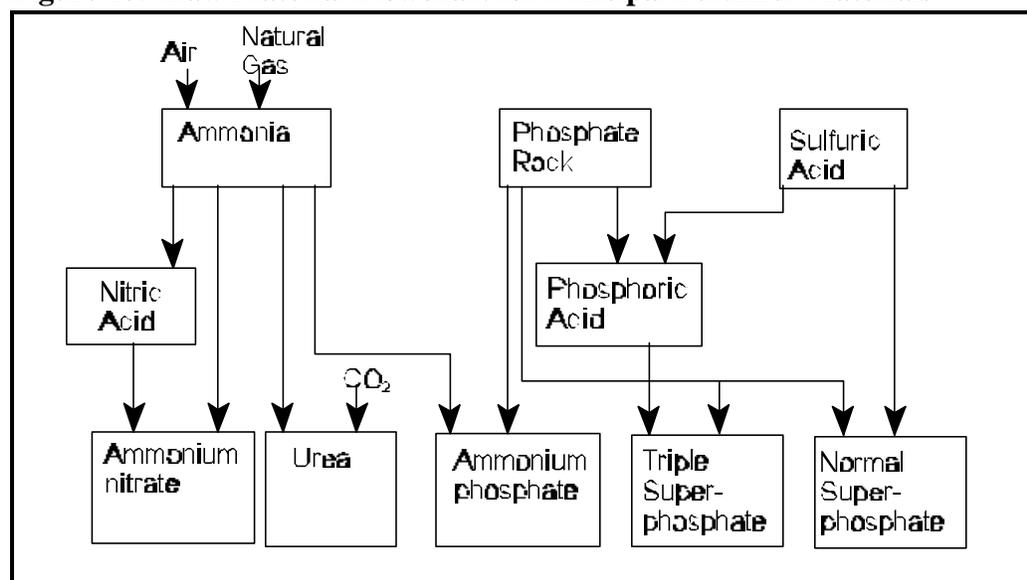
Raw material inputs and pollution outputs of fertilizer products and pesticide products differ considerably, and, therefore, are discussed separately below. The pollution outputs are discussed both specifically by product as well as generally by process since there are some similarities in the fertilizer and pesticide production processes and pollutant outputs.

III.E.1. Fertilizers

The primary raw materials for fertilizer manufacturing are phosphate rock, natural gas, sulfuric acid, and carbon dioxide. These materials are combined by several methods and in different proportions to produce a variety of fertilizer products, as described in section III.

Figure 18 summarizes the fertilizer material inputs for the principal fertilizer products.

Figure 18: Raw Material Flowchart for Principal Fertilizer Materials



Source: Adapted from *Manual on Fertilizer Statistics*, Food and Agriculture Organization of the United Nations, Rome 1991.

Because the basic fertilizer nutrients are found in many natural and manmade materials, raw materials for fertilizers can also be derived from sources other than the virgin materials described above. Common sources of fertilizer ingredients are sewerage treatment sludges and certain industrial wastes. Although these waste-derived fertilizers may contain essentially the same

nutrients as fertilizers derived from virgin materials, they also may contain additional constituents that were present in the waste material and which may not be beneficial, or are potentially harmful to crops, human health, or the environment. Such constituents may enter the food chain or groundwater and could become concentrated in the soil after repeated use. Lead, cadmium and arsenic are some of the more common fertilizer ingredients that could be harmful if sufficient quantities are present. It should be noted, however, that fertilizers derived from virgin materials also have the potential to contain harmful levels of these constituents if significant quantities are naturally present in the raw materials.

One waste material input which has received some attention recently is cement kiln dust (CKD). Although there has been a considerable amount of research conducted on CKD use as a fertilizer, existing applications of CKD for this purpose have been mostly anecdotal, and there is only limited evidence that commercial CKD use as a fertilizer is growing significantly (USEPA, 1993b).

Like agricultural lime, CKD is alkaline and contains a number of essential plant nutrients. Because of these parallel characteristics, CKD has been used as an agricultural soil amendment. CKD possesses significant fertilizer potential, particularly because of its high potassium content. Soil scientists have also suggested that other key plant nutrients contained in CKD, such as calcium, phosphorous, and zinc, might be beneficial in some fertilizer applications. However, some concern has been raised over hazardous wastes in CKD (USEPA, 1993b).

Coal combustion by-products are also receiving attention for their potential agricultural benefits, including alleviating soil trace elemental deficiencies, modifying soil pH, and increasing levels of Ca and S, infiltration rates, depth of rooting, and drought tolerance. Flue gas desulfurization residues, which contain gypsum, have the potential to improve water use efficiency, product quality, and productivity of soil-crop systems. The short term benefits of coal combustion by-products usage has been demonstrated, however, long term effects have not been documented. Future hazards and benefits are yet to be determined (Korcak, 1995). Electric-arc furnace dust is also used as a fertilizer ingredient since it contains a number of trace elements required by plants, including zinc.

Pollution outputs are summarized in terms of air emission, wastewater, and residual wastes.

Air Emissions

Synthetic Ammonia

Air pollutants from the manufacture of synthetic anhydrous ammonia are emitted primarily from four process steps:

- C regeneration of the desulfurization bed,
- C heating of the catalytic steam,
- C regeneration of carbon dioxide scrubbing solution,
- C steam stripping of process condensate.

More than 95 percent of the ammonia plants in the United States use activated carbon fortified with metallic oxide additives for feedstock desulfurization. Vented regeneration steam contains sulfur oxides (SO_x) and hydrogen sulfide (H_2S), depending on the amount of oxygen in the steam. Regeneration may also emit hydrocarbons and carbon monoxide (CO). The reformer, heated with natural gas or fuel oil, may emit combustion products such as NO_x , CO , SO_x , hydrocarbons, and particulates (USEPA, 1993a).

Carbon dioxide (CO_2) is removed from the synthesis gas by scrubbing with monoethanolamine ($\text{C}_2\text{H}_4\text{NH}_2\text{OH}$) or hot potassium carbonate solution. Regeneration of this CO_2 scrubbing solution with steam produces emissions of water, NH_3 , CO , CO_2 and monoethanolamine (USEPA, 1993a).

Cooling the synthesis gas after low temperature shift conversion forms a condensate containing NH_3 , CO_2 , methanol (CH_3OH), and trace metals. Condensate steam strippers are used to remove NH_3 and methanol from the water, and steam from this may be vented to the atmosphere, emitting NH_3 , CO_2 , and methanol (USEPA, 1993a).

Nitric Acid

Emissions from nitric acid manufacturing consist primarily of NO and NO_2 (which account for visible emissions), and trace amounts of HNO_3 mist and NH_3 . The major source of nitrogen oxides is the tail gas from the acid absorption tower. In general, the quantity of nitrogen oxides (NO_x) emissions is directly related to the kinetics of the nitric acid formation reaction and absorption tower design. NO_x emissions can increase when there is:

- C insufficient air supply to the oxidizer and absorber,
- C low pressure, especially in the absorber,
- C high temperatures in the cooler/condenser and absorber,
- C production of an excessively high-strength product acid,
- C operation at high throughput rates,
- C faulty equipment such as compressors or pumps which lead to lower pressures, leaks, and reduced plant efficiency (USEPA, 1993a).

Comparatively small amounts of nitrogen oxides are also lost from acid concentrating plants. These losses (mostly NO_2) are from the condenser system, but the emissions are small enough to be controlled easily by absorbers.

Acid mist emissions do not occur from the tail gas of a properly operated

plant. The small amounts that may be present in the absorber exit gas streams are typically removed by a separator or collector prior to entering the catalytic reduction unit or expander.

The acid production system and storage tanks can be a significant source of visible NO_x emissions at nitric acid plants. Emissions from acid storage tanks are most likely to occur during tank filling (USEPA, 1993a).

Ammonium Nitrate

The primary air emissions from ammonium nitrate production plants are particulate matter (ammonium nitrate and coating materials), ammonia and nitric acid. Ammonia and nitric acid are emitted primarily from solution formation and granulators. Particulate matter (largely as ammonium nitrate) can be emitted from most of the process operations (USEPA, 1993a).

The emission sources in solution formation and concentration processes are neutralizers and evaporators, emitting nitric acid and ammonia. The vapor stream off the top of the neutralization reactor is primarily steam with some ammonia and NH₄NO₃ particulates present. Specific plant operating characteristics, however, make these emissions vary depending upon use of excess ammonia or acid in the neutralizer. Particulate emissions from these operations tend to be smaller in size than those from solids production and handling processes and generally are recycled back to the process (USEPA, 1993a).

Emissions from solids formation processes are ammonium nitrate particulate matter and ammonia. The sources of primary importance are prill towers (for high density and low density prills) and granulators (rotary drum and pan). Emissions from prill towers result from carryover of fine particles and fume by the prill cooling air flowing through the tower. These fine particles are from microprill formation, attrition of prills colliding with the tower or one another, and rapid transition of the ammonia nitrate between crystal states (USEPA, 1993a).

Microprill formation resulting from partially plugged orifices of melt spray devices can increase fine dust loading and emissions. Certain designs (spinning buckets) and practices (vibration of spray plates) help reduce plugged orifices and thus microprill formation. High ambient air temperatures can cause increased emissions because of entrainment as a result of higher air flow required to cool prills and because of increased fume formation at the higher temperatures (USEPA, 1993a).

Emissions from screening operations are generated by the attrition of the ammonium nitrate solids against the screens and against one another. Almost all screening operations used in the ammonium nitrate manufacturing industry are enclosed or have a cover over the uppermost screen. Emissions are ducted from the process for recovery or reuse (USEPA, 1993a).

Bagging and bulk loading operations are also a source of particulate emissions. Dust is emitted from each type of bagging process during final filling when dust laden air is displaced from the bag by the ammonium nitrate. The potential for emissions during bagging is greater for coated than for uncoated material. It is expected that emissions from bagging operations are primarily the kaolin, talc or diatomaceous earth coating matter. About 90 percent of solid ammonium nitrate produced domestically is bulk loaded. While particulate emissions from bulk loading are not generally controlled, visible emissions are within typical state regulatory requirements (below 20 percent opacity) (USEPA, 1993a).

Urea

Emissions from urea manufacture are mainly ammonia and particulate matter. Formaldehyde and methanol, hazardous air pollutants, may be emitted if additives are used. Formalin™, used as a formaldehyde additive, may contain up to 15 percent methanol. Ammonia is emitted during the solution synthesis and solids production processes. Particulate matter is emitted during all urea processes (USEPA, 1993a).

In the synthesis process, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled. Typical emission sources from the solution synthesis process are noncondensable vent streams from ammonium carbamate decomposers and separators. Emissions from synthesis processes are generally combined with emissions from the solution concentration process and are vented through a common stack. Combined particulate emissions from urea synthesis and concentration operations are small compared to particulate emissions from a typical solids-producing urea plant. The synthesis and concentration operations are usually uncontrolled except for recycle provisions to recover ammonia (USEPA, 1993a).

Uncontrolled emission rates from prill towers may be affected by the following factors:

- C product grade being produced
- C air flow rate through the tower
- C type of tower bed
- C ambient temperature and humidity (USEPA, 1993a)

The total of mass emissions per unit is usually lower for feed grade prill production than for agricultural grade prills, due to lower airflows. Uncontrolled particulate emission rates for fluidized bed prill towers are higher than those for nonfluidized bed prill towers making agricultural grade prills, and are approximately equal to those for nonfluidized bed feed grade prills (USEPA, 1993a).

Ambient air conditions can affect prill tower emissions. Available data indicate that colder temperatures promote the formation of smaller particles

in the prill tower exhaust. Since smaller particles are more difficult to remove, the efficiency of prill tower control devices tends to decrease with ambient temperatures. This can lead to higher emission levels for prill towers operated during cold weather. Ambient humidity can also affect prill tower emissions. Air flow rates must be increased with high humidity, and higher air flow rates usually cause higher emissions (USEPA, 1993a).

In the solids screening process, dust is generated by abrasion of urea particles and the vibration of the screening mechanisms. Therefore, almost all screening operations used in the urea manufacturing industry are enclosed or are covered over the uppermost screen. Emissions attributable to coating include entrained clay dust from loading, inplant transfer, and leaks from the seals of the coater (USEPA, 1993a).

Phosphoric Acid

Gaseous fluorides such as silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF) can be major emissions from wet process acid production. Phosphate rock contains 3.5 to 4.0 percent fluorine. Part of the fluorine from the rock is precipitated with the gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporized in the reactor or evaporator. The relative quantities of fluorides in the filter acid and gypsum depend on the type of rock and the operating conditions. Final disposition of the volatilized fluoride depends on the design and operation of the plant (USEPA, 1993a).

The reactor in which phosphate rock is reacted with sulfuric acid is the main source of emissions. Fluoride emissions accompany the air used to cool the reactor slurry. Vacuum flash cooling has replaced the air cooling method to a large extent, since emissions are minimized in the closed system.

Acid concentration by evaporation is another source of fluoride emissions. Approximately 20 to 40 percent of the fluorine originally present in the rock vaporizes in this operation. Particulate matter containing fluorides can be emitted directly from process equipment. About three to six percent of the particulates can be fluorides, as measured at one facility (USEPA, 1993a).

Ammonium Phosphates

The major sources of air emissions from the production of ammonium phosphatic fertilizers include the reactor, the ammoniator-granulator, the dryer and cooler, product sizing and material transfer, and the gypsum pond. The reactor and ammoniator-granulator produce emissions of gaseous ammonia, gaseous fluorides such as hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4), and particulate ammonium phosphates. These two exhaust streams are generally combined and passed through primary and secondary scrubbers (USEPA, 1993a).

Exhaust gases from the dryer and cooler also contain ammonia, fluorides and

particulates, and these streams are commonly combined and passed through cyclones and primary and secondary scrubbers. Particulate emissions and low levels of ammonia and fluorides from product sizing and material transfer operations are controlled the same way (USEPA, 1993a).

Normal Superphosphates

Sources of emissions at a normal superphosphate plant include rock unloading and feeding, mixing operations (in the reactor), storage (in the curing building), and fertilizer handling operations. Rock unloading, handling and feeding generate particulate emissions of phosphate rock dust. The mixer, den and curing building emit gases in the form of silicon tetrafluoride (SiF_4), hydrogen fluoride (HF) and particulates composed of fluoride and phosphate material (USEPA, 1993a).

Triple Superphosphates

Emissions of fluorine compounds and dust particles occur during the production of granulated triple superphosphate. Silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF) are released by the acidulation reaction and they evolve from the reactors, den, granulator, and dryer. Evolution of fluoride is essentially finished in the dryer and there is little fluoride evolved from the storage pile in the curing building (USEPA, 1993a).

Sources of particulate emissions include the reactor, granulator, dryer, screens, cooler, mills, and transfer conveyors. Additional emissions of particulate result from the unloading, grinding, storage, and transfer of ground phosphate rock. Facilities may also use limestone, which is received in granulated form and does not require additional milling (USEPA, 1993a).

Wastewater

Wastewater from the fertilizer industry can be classified into four groups:

- C process effluents resulting from contact with gas, liquids, or solids
- C dedicated effluents which may be separated for use in one process or for recycling at a controlled rate
- C effluents from general services such as cleaning or pretreatment
- C occasional effluents such as leaks or spills

A number of process wastewater streams from the nitrogenous fertilizer industry have been identified. Frequently these wastewaters contain high levels of nitrogenous compounds such as ammonia, nitrates, and organic nitrogen. In ammonia production, wastewater is generated from process condensate stripping. Ammonium nitrate manufacturing produces process wastewater in the neutralization process, the evaporation unit, and air cooling equipment. The vacuum condenser in urea plants is a source of wastewater. Most scrubbing operations are also a source of wastewater. Nitric acid

production generates relatively little wastewater since there is no process wastewater source. Steam generated in nitrogenous fertilizer processing may contain dissolved and suspended solids, alkalinity, and hardness (USEPA, 1974).

The most common methods for removing nitrogenous compounds include:

- C Biological nitrification/denitrification
- C Air or steam stripping
- C Ion exchange
- C Breakpoint chlorination (Water Environment Federation, 1994).

The major source of wastewater from any phosphatic fertilizer manufacturing process is referred to as “pond water.” Phosphoric acid production creates large quantities of pond water for cooling of the process, concentration of the product and for processing and storage of the gypsum byproduct. Gypsum slurry water is decanted from the top of the gypsum stacks and sent to the cooling pond through collection ditches (USEPA, 1993a). Through evaporation and recycling, contaminant concentrations in pond water can reach several grams per liter of phosphates and fluoride. Additional elemental contaminants in pond water which originate in phosphate rock are arsenic, cadmium, uranium, vanadium, and radium (USEPA, 1974).

The most common industry treatment for removing phosphorous is lime neutralization and settling.

Occasional wastewater is generated in any fertilizer production facility by leaks, spills, cleaning, maintenance, and laboratory tests. Cleaning of cooling and pollution control systems also produces process wastewater. Cooling water may contain ammonia, sulfate, chloride, phosphate, chromate, and dissolved solids which become concentrated through evaporation (USEPA, 1974). The laundry of workers' clothing is another source of wastewater originating outside the actual process.

Solid/Hazardous/Residual Wastes

One of the largest solid wastes in the fertilizer industry is phosphogypsum which is produced during phosphoric acid production. Approximately 1.5 tons of phosphogypsum is produced per ton of phosphate rock fed, or 5 tons per ton of phosphoric acid produced (expressed as P_2O_5). Gypsum (calcium sulphate dihydrate) is a mineral which also occurs in nature. Phosphogypsum is produced by the reaction of phosphate rock with sulphuric acid during the process of producing phosphoric acid. The term “phosphogypsum” is used to specify the particular gypsum arising from the acidulation of phosphate rock, because it contains trace amounts of many of the mineral impurities that accompany phosphate rock. One of these impurities is radium, the parent of radon. Other trace impurities found in phosphogypsum include arsenic, nickel, cadmium, lead, aluminum, fluoride, and phosphoric acid. Mainly because of

the radium content, the EPA restricts use of phosphogypsum and stipulates that no phosphogypsum with radium over ten pCi/g can be removed from the stacks adjacent to the agricultural chemical plants (UNEP, 1996).

The use of waste phosphogypsum for other purposes has been widely encouraged, but economic and/or quality problems and/or the demand for the resulting products frequently inhibit or prevent this. These problems relate not only to the impurities in the gypsum, but also to its relatively high moisture content. Plasterboard, plaster, and cement are the main possibilities. It is also possible to recycle phosphogypsum in sulphuric acid production. The ready availability of natural gypsum and the high cost of gypsum-based sulphuric acid, as well as the presence of trace contaminants, are the main obstacles to its use (Miller, 1995). However, in countries where gypsum and other sulphurous raw materials are scarce, phosphogypsum has been successfully used for these purposes (UNEP, 1996).

Dumping gypsum on land is not possible everywhere because the material settles and dries slowly and requires an adequate land area and certain climatic and soil conditions where the stack is situated. Gypsum stacks are being increasingly regulated in terms of lining and cap systems to prevent contaminated leaching or runoff (UNEP, 1996).

All phosphate ores contain traces of radioactive elements and a number of metals. During processing, these are partitioned between beneficiation process wastes, the waste from the further processing into intermediate and finished fertilizer production, and some end up in the final product (UNEP, 1996).

Cadmium is a heavy metal which accumulates in living systems and can become toxic above certain limits. The quantity of cadmium contained in a phosphatic fertilizer depends on the source of the rock or waste material from which it was made. The cadmium content of phosphate rocks varies from almost zero to over 300 mg/kg P₂O₅. The acidulation of phosphate rock partitions the cadmium between the fertilizer product and the by-products, mainly the phosphogypsum arising from phosphoric acid production (UNEP, 1996).

The fertilizer industry has for some decades tried to develop cadmium separation processes. Processes studied so far have shown serious limitations and problems, with regard to safety, cost, energy consumption or environmental concerns. Currently available processes are expensive and are not economically viable except for phosphates destined for human or animal consumption, which have a greater added value. A process developed for removing cadmium from phosphoric acid, which is used in the production of many phosphatic fertilizers (except normal superphosphate), has shown promise on a laboratory scale, but needs further testing before being used on an industrial scale (UNEP, 1996).

Off-specification product, spills, and dusts collected in emission control systems are potential sources of residual wastes. Products are occasionally suspended or canceled, leaving stockpiles of residual product. Other possible sources of solid wastes are spent catalysts, spent containers, wastewater treatment sludges, and spent filters. Many of these wastes are transported off-site for disposal. However, with good housekeeping techniques and dedicated systems, some of these wastes may be recycled back into the process instead of being wasted.

Catalysts used in the steam reforming process need to be replaced every two to six years. Spent catalysts contain oxides of hexavalent chromium, zinc, iron, and nickel. They are typically returned to the manufacturer or other metal recovery companies for recycling and reclamation of valuable materials (UNEP, 1996).

III.E.2. Pesticide Formulating, Packaging, and Repackaging

As listed below, input raw materials include the pesticide concentrates from pesticide manufacturing plants as well as diluents and other chemical additives used in the formulating process:

C Active Ingredients

Organic/inorganic pesticides: insecticides, herbicides, fungicides, and others. (See Table 10.)

C Formulation and preparation materials

Dry formulations:

organic flours, sulfur, silicon oxide, lime, gypsum, talc, pyrophyllite, bentonites, kaolins, attapulgate, and volcanic ash.

Liquid formulations:

Solvents: xylenes, kerosenes, methyl isobutyl ketone, amyl acetate, and chlorinated solvents.

Propellants: carbon dioxide and nitrogen.

Others: wetting and dispersing agents, masking agents, deodorants, and emulsifiers (USEPA, 1990).

In addition to pesticide materials, some facilities listed under SIC code 2879 produce fertilizer/pesticide blends. A variety of nitrogenous, phosphatic, and mixed fertilizers may be inputted into bulk blending tanks to produce these combinations.

Table 10: Approximate Quantities of Most Commonly Used Conventional Pesticides in United States Agricultural Crop Production

Chemical	1995 Consumption (Million pounds active ingredient)	Chemical	1995 Consumption (Million pounds active ingredient)
Atrazine	68-73	Chlorpyrifos	9-13
Metolachlor	59-64	Chlorothalonil	8-12
Metam Sodium	449-54	Copper Hydroxide	7-11
Methyl Bromide	39-46	Propanil	6-10
Dichloropropene	38-43	Dicamba	6-10
2,4-D	31-36	Terbufos	6-9
Glyphosate	25-30	Mancozeb	6-9
Cyanazine	24-29	Fluometuron	5-9
Pendimethalin	23-28	MSMA	4-8
Trifluralin	23-28	Bentazone	4-8
Acetochlor	22-27	Parathion	4-7
Alachlor	19-24	Sodium Chlorate	4-6
EPTC	9-13		

Source: Pesticide Industry Sales and Usage, 1994 and 1995 Market Estimates, EPA, August 1997.

Air Emissions

Air emissions can be generated throughout the pesticide formulating and packaging processes, mostly when fine particulates of pesticide dust become suspended in air while the materials are being moved, processed, or stored. Most dust or granule blending mills are equipped with vacuum systems, cyclones, and wet scrubbers to collect fugitive dust. Some vacuum systems are dedicated to certain processes to facilitate reuse of the dust. Other systems are used to collect dust from a number of areas (USEPA, 1990). Dust generated by pesticide formulation processes contain AIs which may be toxic to humans and the environment. Thus, they are important to contain.

Volatile organic compound (VOC) emissions such as xylene may also arise when solvent-based liquid formulations are produced. VOC emissions may also be generated during equipment cleaning with solvents.

Wastewater

Process wastewater is defined in 40 CFR 122.2 as “any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, byproduct, intermediate product, finished product, or waste product.” Wastewater from the pesticide formulating industry is typically due to cleaning of equipment and related process areas and not the actual formulating processes (USEPA, 1996).

Cleaning and decontaminating blending and liquid pesticide mixing and storage equipment generates pesticide-contaminated wastewater or solvent, depending upon whether the equipment is used to formulate water or solvent-based pesticides. Decontamination is performed between batches of different types of formulations to prevent cross contamination of the subsequent batch. Decontamination is also performed prior to taking the equipment out of service for maintenance. The decontamination is commonly performed using high pressure water hoses equipped with spray nozzles, portable steam generators, or by running a batch of solvent through the formulating equipment (USEPA, 1990).

Active ingredient containers, such as 55-gallon drums, are often decontaminated by triple rinsing. The decontamination is usually performed using a high pressure water hose equipped with a spray nozzle or a portable steam jenny. The containers can then be sold or given to commercial recycling firms, depending on label directions (USEPA, 1990).

Floor, wall, and equipment exterior washing is typically performed using water hoses equipped with spray nozzles. It may also involve the use of mops and squeegees. Wastewater is also generated by clean-up of spills and leaks.

Wastewater from these operations typically contains AIs, solvents, and wetting agents (USEPA, 1990). Other sources of wastewater include:

- C Pollution control scrubber water
- C Department of Transportation leak test water
- C Safety equipment wash water
- C Laboratory equipment wash water
- C Shower water
- C Laundry water
- C Fire protection test water
- C Contaminated precipitation runoff (USEPA, 1996)

Solid/Hazardous/Residual Wastes

Residual wastes include containers and container liners potentially contaminated with pesticides, as well as off-spec product, dust collected from

emission control equipment, and product spills. Contaminated laboratory equipment and protective workers clothing are other potential solid waste sources (USEPA, 1990).

Decontamination of the solid-based pesticide blending mills may generate solid diluent contaminated with pesticides. The diluent typically consists of clay for dust mills and sand for granule mills (USEPA, 1990).

In case of pesticide products which have been suspended or canceled, there may be existing stocks of these products remaining. EPA may allow the use of existing stocks or prohibit such use. State environmental agencies occasionally collect unusable pesticides.

Procedures for pesticide management have been proposed by EPA, as authorized under section 19 of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). For more details, refer to section VI.C on pending and proposed regulatory requirements.

Table 11: Summary of Potential Pollution Outputs for the Agricultural Chemical Industry			
Process	Air Emissions	Process Wastewater	Residual Waste
Nitric Acid Absorption Tower	NO, NO ₂ , HNO ₃ in tailgas	NA	Spent tower materials, trays
Solution Formulation and Granulation	NH ₃ , HNO ₃ particulates	Condensed steam with NH ₄ NO ₃ and NH ₃	NA
Solids Formation	Particulates, NO _x , SiF ₄ , HF	NA	Dusts
Regeneration of Desulfurization and Filter Beds	Hydrocarbons, CO, NH ₃ , CO ₂	Condensed steam, NH ₃ , CO ₂	Spent bed material
Screening	Dust	NA	Mixed undersized captured dusts, used screens
Wet Process Phosphoric Acid Production	SiF ₄ , HF	Pond water	Gypsum
Unloading of materials into blending tanks	Dust/particulates released in transfer	NA	Leftover raw material containers
Open processing and storage equipment	VOC's	NA	NA
Equipment and facility cleaning	NA	Washwater, waste solvent	Waste sands and clays, used mops/squeegees/etc.
Laboratory procedures	VOC's and dusts released	Washwater, lab testing water	Off-spec product used for testing/analysis
Spills and runoff	Dust/particulates released by spill	Contaminated rainfall/runoff	Contaminated solid product
Pollution control systems	NA	Contaminated scrubber water	Spent filter material

Source: Guide to Pollution Prevention, The Pesticide Formulating Industry, Center for Environmental Research Information, United States EPA, Washington D.C., 1990.

III.F. Management of Chemicals in Wastestream

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of Toxic Release Inventory (TRI) chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in section 8 of the TRI reporting Form R beginning with the 1991 reporting year. The data summarized below cover the years 1995-1998 and are meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention or compliance assistance activities.

While the quantities reported for 1995 and 1996 are estimates of quantities already managed, the quantities listed by facilities for 1997 and 1998 are projections only. The PPA requires these projections to encourage facilities to consider future source reduction, not to establish any mandatory limits. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Fertilizers

Table 12 shows that the TRI reporting fertilizer manufacturing and mixing facilities managed about 566 million pounds of production related wastes (total quantity of TRI chemicals in the waste from routine production operations in column B) in 1996. From the yearly data presented in column B, the total quantity of production related TRI wastes decreased between 1995 and 1996. Production related wastes are projected to increase in 1997 and 1998. Note that the affects of production increases and decreases on the quantities of wastes generated are not evaluated here.

In 1996, about 84 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns C, D, and E, respectively. Most of these on-site managed wastes were recycled on-site. There is a negligible amount (<1%) of wastes being transferred off-site for recycling, energy recovery, or treatment. The remaining portion of the production related wastes (12 percent in 1995 and 16 percent in 1996), shown in column I, is either released to the environment through direct discharges to air, land, water, and underground injection, or is transferred off-site for disposal.

Table 12: Source Reduction and Recycling Activity for the Fertilizer Industry as Reported within TRI								
A	B	On-Site			Off-Site			I
Year	Quantity of Production-Related Waste (10 ⁶ lbs.) ^a	C	D	E	F	G	H	% Released and Disposed ^c Off-site
		% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated	
1995	719	76%	8%	4%	0%	0%	0%	12%
1996	566	77%	1%	6%	0%	0%	0%	16%
1997	606	77%	1%	7%	0%	0%	0%	15%
1998	617	78%	1%	7%	0%	0%	0%	14%

Source: 1996 Toxics Release Inventory Database.

^a Within this industry sector, non-production related waste < 1% of production related wastes for 1996.

^b Total TRI transfers and releases as reported in section 5 and 6 of Form R as a percentage of production related wastes.

^c Percentage of production related waste released to the environment and transferred off-site for disposal.

Pesticides and Miscellaneous Agricultural Chemicals

Table 13 shows that the TRI reporting pesticide and miscellaneous agricultural chemicals facilities managed about 252 million pounds of production related wastes (total quantity of TRI chemicals in the waste from routine production operations in column B) in 1996. From the yearly data presented in column B, the total quantity of production related TRI wastes increased between 1995 and 1996. Production related wastes were projected to continue to increase in 1997 and 1998. Note that the affects of production increases and decreases on the quantities of wastes generated are not evaluated here.

In 1996, about 95 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns C, D, and E, respectively. Most of these on-site managed wastes were recycled on-site. A small portion of the remaining wastes (4% in 1996) are transferred off-site for recycling, energy recovery, or treatment. The remaining one percent of the production related wastes, shown in column I, is either released to the environment through direct discharges to air, land, water, and underground injection, or is transferred off-site for disposal.

Table 13: Source Reduction and Recycling Activity for the Pesticide and Miscellaneous Agricultural Chemicals Industry as Reported within TRI								
A	B	On-Site			Off-Site			I
Year	Quantity of Production-Related Waste (10 ⁶ lbs.) ^a	C	D	E	F	G	H	% Released and <u>Disposed</u> ^c Off-site
		% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated	
1995	245	85%	0%	10%	2%	1%	1%	2%
1996	252	84%	0%	11%	2%	1%	1%	1%
1997	266	84%	0%	11%	1%	1%	2%	1%
1998	279	85%	0%	11%	1%	1%	1%	1%

Source: 1996 Toxics Release Inventory Database.

^a Within this industry sector, non-production related waste < 1% of production related wastes for 1996.

^b Total TRI transfers and releases as reported in section 5 and 6 of Form R as a percentage of production related wastes.

^c Percentage of production related waste released to the environment and transferred off-site for disposal.

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